Bandgap Renormalization in Monolayer MoS$_2$ on CsPbBr$_3$ Quantum Dots via Charge Transfer at Room Temperature

Subash Adhikari, Ji-Hee Kim,* Bumsub Song, Manh-Ha Doan, Minh Dao Tran, Leyre Gomez, Hyun Kim, Hamza Zad Gul, Ganesh Ghimire, Seok Joon Yun, Tom Gregorkiewicz, and Young Hee Lee*

Many-body effect and strong Coulomb interaction in monolayer transition metal dichalcogenides lead to intrinsic bandgap shrinking, originating from the renormalization of electrical/optical bandgap, exciton binding energy, and spin-orbit splitting. This renormalization phenomenon has been commonly observed at low temperature and requires high photon excitation density. Here, the augmented bandgap renormalization (BGR) in monolayer MoS$_2$ anchored on CsPbBr$_3$ perovskite quantum dots at room temperature via charge transfer is presented. The amount of electrons significantly transferred from perovskite gives rise to the large plasma screening in MoS$_2$. The bandgap in heterostructure is red-shifted by 84 meV with minimal pump fluence, the highest BGR in monolayer MoS$_2$ at room temperature, which saturates with a further increase of pump fluence. Further, it is found that the magnitude of BGR inversely relates to Thomas–Fermi screening length. This provides plenty of room to explore the BGR within existing vast libraries of large bandgap van der Waals heterostructure toward practical devices such as solar cells, photodetectors, and light-emitting-diodes.

1. Introduction

Reduction of optical and/or electrical bandgap by quantum confinement Stark effect$^{[1–4]}$ and Coulomb screening$^{[5–10]}$ has been the subject of interest in 2D van der Waals (vdW) materials. For example, the Stark effect reduces the optical bandgap in MoS$_2$ upon application of uniform electric field,$^{[3,4]}$ while the Coulomb interaction by dielectric/plasma screening modifies the overall band structure of 2D semiconductors.$^{[7,11]}$ This leads to optical and/or electrical bandgap renormalization (BGR), a carrier density-dependent shrinkage of the bandgap.$^{[12–15]}$

Bandgap modification in 2D semiconductors can also be obtained using mechanical strain,$^{[16–20]}$ which is not highly desirable owing to the strain sensitivity.$^{[21,22]}$ Meanwhile, Coulomb engineering by dielectric/plasma screening using either dielectric materials (2D and bulk) or free carriers from external sources (charge doping, photoexcitation, and electric field) offers a non-perturbative and nanoscale control of electrical and optical bandgaps,$^{[9,11,23–28]}$ which is advantageous over the strain. In particular, monolayer WS$_2$ on hexagonal boron nitride (hBN) under large electron doping reveals the spin-orbit splitting, resulting in the BGR of $\approx$325 meV$^{[20]}$ while the dielectric screening with graphene on monolayer WS$_2$ reduces electronic bandgap by more than 100 meV.$^{[24]}$ However, these phenomena are observed only at low temperature while room temperature phenomena requires high photoexcitation fluence/density.$^{[25]}$ Similarly, the optical BGR in monolayer MoS$_2$ under high photoexcitation at low temperature is shifted by 30–50 meV$^{[23]}$ and the bandgap in MoS$_2$/hBN is reduced from 400 meV at femtosecond time scale to <100 meV in picoseconds time range.$^{[31]}$

Coulomb engineering with dielectric patterning thus allows for the selective reduction of the bandgap by renormalization phenomenon at nanoscale resolution. More importantly, BGR can offer several possibilities in wide bandgap vdW materials for the development of near-infrared (NIR) optical/opto-electronic devices. However, the electrical/optical BGR shift with dielectric/plasma screening either requires an optical excitation source with high photoexcitation density, and/or are observed mostly at low temperature (summarized in Table S1, Supporting Information). The high photoexcitation also produces structural/phase transition as well as higher order exciton interaction in 2D materials which limits the practical applications of BGR phenomenon for large bandgap reduction in monolayer vdW materials.$^{[25,29–31]}$ The challenge is to achieve tunable electronic structure modifications of large bandgap vdW materials.

Dr. S. Adhikari, Prof. J.-H. Kim, B. Song, Dr. M.-H. Doan, Dr. M. D. Tran, Dr. H. Kim, Dr. H. Z. Gul, G. Ghimire, Dr. S. J. Yun, Prof. Y. H. Lee
IBS Center for Integrated Nanostructure Physics
Institute for Basic Science (IBS)
Sungkyunkwan University
Suwon 440-746, Republic of Korea
E-mail: kimj@skku.edu; leeyoung@skku.edu

Dr. S. Adhikari, Prof. J.-H. Kim, B. Song, Dr. M.-H. Doan, Dr. M. D. Tran, Dr. H. Kim, Dr. H. Z. Gul, G. Ghimire, Dr. S. J. Yun, Prof. Y. H. Lee
Department of Energy Science
Department of Physics
Sungkyunkwan University
Suwon 440-746, Republic of Korea

Dr. L. Gomez, Prof. T. Gregorkiewicz
Van der Waals–Zeeman Institute
University of Amsterdam
Science Park 904, Amsterdam 1098 XH, Netherlands
The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/admi.202000835.

DOI: 10.1002/admi.202000835
at room temperature and with a low photoexcitation density to realize a robust BGR shift for the development of transition metal dichalcogenides based electronic/optoelectronic devices.

In this study, we demonstrated BGR at room temperature via interfacial electron transfer in the type-II hybrid structure of MoS$_2$, and all-inorganic CsPbBr$_3$ perovskite quantum dots (PQDs). This was achieved from the shift of the optical bandgap as revealed by optical characterization by linear absorption, photoluminescence (PL), and transient absorption (TA). The efficient charge transfer from PQDs to MoS$_2$, further enhanced by the photoexcitation of highly absorbing and luminescent PQDs, allows for the carrier density in MoS$_2$ as high as $7.7 \times 10^{12} \text{cm}^{-2}$ giving rise to enhanced plasma screening effect in PQD/MoS$_2$ heterostructure. Our heterostructure charge transfer-based renormalization phenomenon resulting in a large BGR shift of 84 meV with a low photon excitation density further demonstrates the feasibility of reducing the optical/electrical bandgap in vdW materials by tailoring the carrier concentration.

2. Results and Discussion

Various photo-induced processes in semiconductors are schematically illustrated in Figure 1. The excited photon energy creates electron-hole pairs with strong exciton binding energy ($E_{\text{ex}}$) typically in monolayer vdW-layered materials, distinct from a quasiparticle bandgap ($E_{\text{gap}}$) (Figure 1a), which is in general indistinguishable from conventional bulk semiconductors at room temperature. Disorder or exciton delocalization can induce binding energy shift, that is, the Stokes shift ($\Delta_{\text{Stokes}}$) (Figure 1b). Similarly, an external electric field can also induce charge dipoles that modulate the exciton binding energy, known as the quantum-confined Stark effect ($\Delta_{\text{Stark}}$). This effect is particularly prominent in quantum-confined structures (Figure 1c). Further, high carrier injection, and/or photoexcitation may produce heavily degenerated situation when the Fermi level moves into the conduction or valence band. In this case, the band filling effect can induce many-body phenomena that renormalize the band structure, resulting in BGR.

All inorganic perovskite crystals with high air stability, large absorption coefficient, and high quantum efficiency can be synthesized with varying chemical compositions and size yielding different bandgaps.$^{[32-37]}$ Among these, pure (20 mg mL$^{-1}$) CsPbBr$_3$ PQDs synthesized by wet-chemistry methods (see Experimental Section for details of synthesis procedure) show a sharp excitonic feature of absorption at 2.426 eV (Figure 2a), and a narrow PL peak at 2.412 eV, producing a Stokes shift of $\approx 14$ meV. This direct bandgap feature in PL with an full width at half maximum (FWHM) of $\approx 80$ meV has been observed for PQDs with size distribution of 11 $\pm$ 2 nm, as shown in the transmission electron microscope (TEM) image together with electron diffraction patterns in the inset.$^{[32,35,36]}$ Figure 2b shows two absorption peaks, A at 1.922 eV, and B-excitons at 2.050 eV in a large-area monolayer MoS$_2$ film synthesized by chemical vapor deposition (CVD) method and transferred onto a quartz substrate (see Experimental Section for details of the growth and transfer process). The PL for the same MoS$_2$ film excited at 2.331 eV (532 nm) is dominated by the neutral exciton ($A_0^+$) peak at 1.929 eV.

The PQD/MoS$_2$ hybrid structure (deposited by spin-coating) (Figure 2c) shows a dominant PL peak at 1.871 eV, corresponding to a negative trion ($A_-$), with a shoulder emission of $A_0^+$ at 1.912 eV (see Figure S1, Supporting Information for the details of the PL mapping image and fitting of PL spectra). This redshift of PL peak position together with the shift of spectral weight in the hybrid structure is attributed to the photo-induced electron transfer,$^{[38,39]}$ more importantly from PQDs to MoS$_2$ in our heterostructure.$^{[40]}$ This is further verified by the out-of-plane $A_{1g}$ peak shift (2.47 cm$^{-1}$) in Raman measurement (see Figure S2, Supporting Information).$^{[40,41]}$ Moreover, the two exciton absorption peaks (A and B-excitons) of MoS$_2$ at 1.899, and 2.03 eV are redshifted in the hybrid structure by $\approx 23$ and

![Figure 1](https://www.advancedsciencenews.com/)  
**Figure 1.** Schematic illustration of emission shift in semiconductor: a) Optical excitation followed by emission via the exciton energy level in semiconductor. b) Stokes shift invoked from disorder or exciton delocalization. c) External electric field (or source-drain voltage) yields quantum confined Stark effect. d) High carrier injection and/or optical excitation generate band filling and BGR.
≈20 meV, respectively, compared to pristine MoS₂ absorption, while the absorption peak of the PQDs in the hybrid structure coincides with that of pristine PQDs (Figure 2a–c and Figure S3, Supporting Information). This absorption shift could originate from either the quantum-confined Stark effect owing to the electric field induced by the interface dipoles in the heterostructure or BGR owing to band filling, as depicted in Figure 1.

Our hybrid structure of PQD/MoS₂, having an electron affinity of 3.8 eV in the PQDs[42,43] and 3.92 eV in MoS₂,[44–46] constructs the staggered band alignment (type-II) (Figure 2d). This creates band bending at the PQD/MoS₂ interface that allows the transfer of electrons (holes) into MoS₂ (PQDs), and is verified by measuring the transfer characteristics of backgated MoS₂ FET (a Hall bar structure shown in the inset) with/without PQDs at \( V_{DS} = 1 \) V (Figure 2e). The pristine MoS₂ reveals intrinsic n-type characteristics with a strong gate modulation and a threshold voltage \( V_{th} \) of 4 V from the linear current (see Figure S4a, Supporting Information). Meanwhile, the \( V_{th} \) is downshifted to \(-28 \) V in the PQD/MoS₂ device. This large negative \( V_{th} \) shift and the increase in \( I_{DS} \) by approximately six orders of magnitude implies a more severe n-doping effect in MoS₂ owing to the charge transfer at the interface.

We estimated the electron concentration \( n \) in PQD/MoS₂ using \( n = q^{-1}C_e\Delta V_{th} = 2.5 \times 10^{12} \) cm\(^{-2}\), where \( q \) is the electron charge, and \( C_e \) is the gate oxide capacitance \((1.23 \times 10^{-8} \) F cm\(^{-2}\)) for 300 nm SiO₂, and \( \Delta V_{th} (-32 \) V) is the shift in the threshold voltage after electron doping from the PQDs.[47,48] This increase of \( n \) in PQD/MoS₂ is also measured quantitatively from the Hall bar measurement at a magnetic field of ≈8 to 8 T (see Figure S4b, Supporting Information for details), thereby yielding a similar electron concentration of \( \Delta n = 2.4 \times 10^{12} \) cm\(^{-2}\).

The observed PL shift together with the electrical measurements suggests that in the hybrid structure the electron concentration in MoS₂ is increased due to charge transfer induced by band alignment at the interface.

To confirm electron transfer from the PQD to MoS₂, we compare the PL intensity mapping (Figure 3a) of the PQDs on quartz, and MoS₂ region (dashed blue area) at an excitation energy of 3.062 eV (405 nm) (see Figure S5a,b, Supporting Information for PL peak position and FWHM mapping). The PQD PL intensity map clearly demonstrates the PL quenching on MoS₂ region. The average PL intensity of PQD on the MoS₂ region decreases approximately by 13 times, compared to the PL intensity on the quartz region (Figure 3b). The quenching of intensity of the PQDs PL in MoS₂ region is readily explained by the electron transfer from the PQDs to MoS₂.[40] This electron transferred on MoS₂ thus produces the redshift as well as intensity quenching in the PL spectra of PQD/MoS₂ (Figure 3b, inset).[38,39] Moreover, no appreciable energy shift nor intensity quenching was observed in a diluted PQD sample (see Figure S6, Supporting Information).

Furthermore, the large electron population from the PQDs in the heterostructure by the electron transfer yields A⁻ with an energy redshift of 50 meV as a consequence of quenched
A0 exciton as well as similar B exciton shift of 40 meV (see Figure S7, Supporting Information for details of PL analysis). The time-dependent PL and current–voltage (I–V) measurement also rules out the possibility of photo-induced charging effect in our heterostructure, suggesting the presence of both, interfacial charge transfer at dark state, and consistent photo-induced charge transfer phenomenon under illumination (see Figure S8, Supporting Information). We also verified the photo-induced charge transfer from the PQDs to MoS2 (Figure 3c) by using time resolved photoluminescence (TRPL) mapping acquired at the PQD PL peak position of 2.412 eV. The fluorescence lifetime of PQDs on MoS2 (dashed blue regions) shows the decrease of lifetime as compared to PQDs on quartz (see Figure S9, Supporting Information for the TRPL spectra and analysis). This is due to the electron transfer from PQDs to MoS2 that decreases the electron density in PQDs thereby reducing the fluorescence lifetime. Hence, both the PL, and TRPL measurement confirms the photoinduced charge transfer phenomenon in the heterostructure. However, the significant shift of position, and spectral weight in A- as well as B-exciton in steady state absorption (Figure 2c) and PL measurement (Figure 2b,c and Figure 3a,b) in the heterostructure, suggests additional phenomenon apart from interfacial and photo-induced charge transfer from PQD to MoS2.

To elucidate the effective many-body phenomena that result in the large energy shift, we measured spectrally-resolved TA maps for MoS2, PQDs, and their heterostructures using a pump energy of 3.543 eV (350 nm) at 22 µJ cm−2 as a function of probe energy and delay time (Figure 4a). The TA map of MoS2 (top image) shows photobleaching (PB, negative absorption) of A-exciton at 1.910 eV and B-exciton at 2.058 eV, while that of the PQDs (middle) shows PB at 2.440 eV. The energy of each exciton peak in TA is similar to that in steady-state absorption (Figure 2b). However, in the PQD/MoS2 heterostructure (bottom image), the A- and B-exciton absorption peaks at an early time delay of 0.3 ps is redshifted (∆Ep) by 82 meV for A-exciton (∆Ep, black dashed line), and 78 meV for B-exciton (∆Ep, gray dashed line) compared to MoS2 throughout the probe delay range. Here, both MoS2, and PQD/MoS2 absorption at a probe delay of 0.2 to 100 ps shows a small blue shift of 10–15 meV due to exciton-phonon scattering (see Figure S10, Supporting Information). Similarly, the photo-induced absorption (PIA) peaks in the PQD/MoS2 heterostructure is also redshifted by 52 meV compared to pristine MoS2 (∆IA, marked by dashed green lines), while it has a small redshift of 17 meV for PQD on MoS2 (red dashed line). The redshift of absorption processes in both A- and B-exciton and the corresponding shift induced by this in the PIA band suggests the renormalization of the whole band structure of MoS2. This absorption peak shift originates from BGR mediated by the band filling effect in MoS2 through a photo-excited charge transfer from the PQDs as well as pump-induced photoexcitation in MoS2.

Figure 3. PL and charge transfer characteristics of PQD: a) PL intensity mapping of PQDs on quartz and MoS2 (dashed blue line) region. Excitation energy was 3.062 eV (405 nm) in the inset with the light blue arrow in the absorption schematic. b) The PL spectra obtained from the MoS2 and quartz region in (a). Inset shows the PL spectra of MoS2 and PQD/MoS2 under the same excitation source with arrow indicating the amount of A-exciton redshift. c) Fluorescence lifetime image of PQDs on quartz and MoS2 (blue dashed line) region. The color scale bar represents the fluorescence lifetime of PQDs.
quasiparticle bandgap, as schematically shown in Figure 4c. Similarly, the carriers accumulated by high fluence further to B-excitons produces plasma screening in A-excitons, consequently modulating the energy redshift or BGR. We note that such a tenable energy shift in the B-excitons at high fluence is not highly appreciable in the A-excitons in our system.

The energy redshift owing to BGR in the PQD/MoS2 heterostructure can also be correlated with the PL. Figure 5a shows the PL spectra of MoS2 at different pump power using an excitation source of 3.062 eV (405 nm) (see Figure S12, Supporting Information for further details of PL). At the lowest power of 10 µW, the PL spectrum of MoS2 shows that A-exciton is composed of dominant neutral excitons (\(\text{MoS}_2^0\)) at 1.918 eV, and a negative trion (\(\text{MoS}_2^-\)) at 1.881 eV owing to intrinsic n-doping in MoS2. This PL spectra at high power (≈96 µW) is primarily dominated by negative trions at 1.870 eV, which is attributed to the increased photon carrier density. In contrast, PQD/MoS2 at 10 µW shows the red-shifted PL spectra dominated entirely by the negative trion (\(\text{PQD/MoS}_2^-\)) at 1.852 eV (Figure 5b), largely by the photoexcited charge transfer from the PQDs as discussed before. At a higher excitation power, \(\text{PQD/MoS}_2^-\) is slightly red-shifted further by maintaining a similar spectral feature at 1.841 eV at ≈96 µW. Similarly, the PL intensity of B-exciton becomes prominent gradually with increasing excitation power, and the energy redshift.

The energy redshift of A-exciton (\(\Delta A = A_{\text{MoS}_2} - A_{\text{PQD/MoS}_2}\)) and similarly that of \(\Delta B\) exciton from the PL spectra are extracted along with \(\Delta E_x\) from TA at the similar excitation energy and power range (Figure 5c and see Figures S13 and S14, Supporting Information for details of TA). Both \(\Delta A\) and \(\Delta B\) in the PL and TA demonstrate the increasing \(\Delta E_x\) with the power that is nevertheless faintly larger for TA. This is ascribed to the additional photo-induced plasma effect in TA, producing \(\Delta A\) of 73 meV for TA as compared to 69 meV in PL at ≈80 µW. The exciton energy redshift by photo-induced charge transfer from PQDs was also analyzed using a laser excitation source of 2.331 eV (532 nm), producing A-exciton renormalization in PQD/MoS2 by 61 meV as well as absorption spectrum producing \(\Delta A\) of 18 meV (see Figures S15–S17, Supporting Information for details of PL, TA, and linear absorption analysis). This confirms the interfacial charge transfer from PQD to MoS2 in the heterostructure, consequently producing the charge-transfer-mediated optical BGR in PQD/MoS2 heterostructure.

The charge-transfer-mediated exciton energy level shift in PQD/MoS2 heterostructure were further studied by scanning tunneling microscopy/spectroscopy (STM/S; see Experimental Section for details regarding the measurements). The Fermi level from STS was shifted by ≈36 meV in MoS2 after PQD deposition (see Figures S18 and S19, Supporting Information), which confirms the interfacial charge transfer from PQD to MoS2 in the heterostructure.

**Figure 4.** TA spectroscopy for BGR analysis in PQD/MoS2 heterostructure: a) Spectrally- and temporally-resolved TA maps for MoS2 (top), PQD (middle), and PQD/MoS2 (bottom). The color scale bar represents the intensity of the A and B-exciton bleach in optical density (mOD). The pump energy was 3.543 eV (350 nm), indicated by the arrow in the inset, with a fluence of 22 µJ cm⁻². b) The dashed lines represent the redshift of induced absorption and exciton energy levels in the heterostructure from their initial positions in MoS2 and PQD. The data are plotted with varying pump fluences. The light blue region represents the maximum A- and B-exciton redshifts and the error bars in the shift are obtained from fitting of the TA spectra. c) Schematic illustration of energy shift through various energy states at low and high pump fluences.
the heterostructure. This charge transfer thus lowers the conduction band minimum in PQD/MoS2 by charge screening (or band filling) effect, giving rise to the electronic bandgap renormalization in PQD/MoS2 heterostructure. More importantly, the decrease of conduction band minimum in STS (≈36 meV) is consistent with the interfacial charge-transfer-mediated optical BGR of exciton energy level shift (ΔA = 18 ± 10 meV) in linear absorption (Figure S17, Supporting Information). This further confirms the optical energy level shift and exciton binding energy reduction originating from electrical BGR.

We finally explain the plasma screening effect described with BGR in terms of the Thomas–Fermi (TF) screening length. The transfer characteristics of the MoS2 FET (Figure 6a) were measured for the photocurrent in MoS2 and PQD/MoS2 heterostructure in the dark and under an excitation energy of 3.062 eV (405 nm) at 134 µW (see Experimental Section and Figure S20 for details of the photocurrent measurement). The MoS2 FET in dark reveals an n-type behavior with a high on/off ratio of 106 and Vth of ≈11 V from the linear current (see Figure S21, Supporting Information). With the addition of PQDs, the drain current (ID) increases, and shifts the Vth to around −23 V owing to the charge transfer from the PQDs (observed before in Figure 1e). The MoS2 FET under laser illumination shows a further increase in n-doping effect with the reduced on/off ratio (≈105) by photo-induced electrons and Vth at around −31 V. Meanwhile, the on/off ratio of the illuminated PQD/MoS2 heterostructure decreases to 104 with a Vth of about −89 V. This high n-doping in the heterostructure originates from the additional charge transfer from the photoexcited electron from the PQDs to MoS2.

Supporting Information for details of the photocurrent measurement. The MoS2 FET in dark reveals an n-type behavior with a high on/off ratio of 10^6 and Vth of ≈11 V from the linear current (see Figure S21, Supporting Information). With the addition of PQDs, the drain current (Id) increases, and shifts the Vth to around −23 V owing to the charge transfer from the PQDs (observed before in Figure 1e). The MoS2 FET under laser illumination shows a further increase in n-doping effect with the reduced on/off ratio (≈10^5) by photo-induced electrons and Vth at around −31 V. Meanwhile, the on/off ratio of the illuminated PQD/MoS2 heterostructure decreases to 10^4 with a Vth of about −89 V. This high n-doping in the heterostructure originates from the additional charge transfer from the photoexcited electron from the PQDs to MoS2.

From the shift of Vth values from the MoS2 position, we also calculated the 2D electron density, and hence the TF screening

Figure 5. Correlation of PL and exciton energy redshift: a,b) Normalized PL of MoS2 (a) and PQD/MoS2 (b) at various laser powers. The solid dots indicate the spectral shift and peak intensity of neutral exciton and negative trions in MoS2 and PQD/MoS2. c) The energy redshift of A- and B-excitons obtained from PL and TA with 3.062 eV (405 nm) excitation source at various powers. The error bars in the shift are obtained from fitting of the TA spectra.
length using \( n = \frac{q^{-1}C_g|\Delta V_{th}|}{\varepsilon \rho T} \) and \( L_{TF} = \left( \frac{e\rho T}{e^2n} \right)^{1/2} \), where \( \varepsilon = \varepsilon_r \varepsilon_0 \) is the dielectric constant, \( \rho \) is the Boltzmann constant, \( T \) is the temperature, \( e \) is the electronic charge, and \( n \) is \( n/t \), with \( t \) being the thickness of monolayer MoS\(_2\) (see Figure 6b and Figure S22, Supporting Information for details).[47–49]

Here, the decrease of TF screening length with electron density is attributed to the plasma screening effect in PQD/MoS\(_2\) heterostructure.[9,11,25,28] Similarly Figure 6c displays the energy redshift of A-exciton (\( \Delta A \)), plotted against the electron concentration obtained from Figure 6a. The values of \( \Delta A \) for PQD/MoS\(_2\)/dark (interfacial charge transfer) was obtained from linear absorption mapping in Figure S17g,h, Supporting Information and for MoS\(_2\)/light and PQD/MoS\(_2\)/light (photo-excited charge transfer) from PL shift in Figure S12e, Supporting Information with 3.062 eV (405 nm) excitation energy at 134 \( \mu \)W.

The obtained \( \Delta A \) is well fitted with carrier density as \( n^{4/3} \) from a model.[30] In addition, the excitonic bandgap renormalization of 18 \( \pm \) 10 meV for PQD/MoS\(_2\) at dark (Figure 6c) due to interfacial charge transfer is consistent with the electrical bandgap renormalization of \( \approx 36 \) meV obtained from STM/S analysis (blue star in Figure 6c and see details in Figures S18d, S19b,e, Supporting Information).

We correlate the optical bandgap renormalization with TF screening length in Figure 6d. Our charge-transfer-mediated optical BGR is inversely related to TF screening length (\( \Delta A \approx L_{TF}^{-8/3} \)) as suggested by \( L_{TF} \propto n^{-1/2} \) and \( \Delta A \propto n^{-4/3} \). The optical BGR induced by interfacial charge transfer in the heterostructure and further enhanced by photoexcited charge transfer in PQD/MoS\(_2\) is ascribed to the enhanced plasma screening effect. This diminishes the mean free path of electrons in PQD/MoS\(_2\) as well as the coulomb interaction of charges in the heterostructure. This leads to conclude that the magnitude of optical bandgap renormalization can be tailored by carrier concentration in van der Waals heterostructures.

3. Conclusions

We have demonstrated the BGR phenomenon in the perovskite/MoS\(_2\) heterostructure mediated by a charge transfer. CsPbBr\(_3\) PQDs can induce electron doping on MoS\(_2\) with a type-II band alignment. The photoexcitation of the PQDs and MoS\(_2\) together with the electron doping by charge transfer produces the plasma screening effect, consequently giving rise to BGR in MoS\(_2\). The increased electron concentration in MoS\(_2\) in a heterostructure, with photoexcitation of PQD reveals a large BGR of 84 meV compared to the BGR of 18 meV by a simple charge transfer in the heterostructure. The observed BGR in MoS\(_2\) by charge-transfer offers various possibilities for reducing the large bandgap of existing vast libraries in van der Waals materials for optoelectronics devices including transistors, solar cells, and photodetectors.
4. Experimental Section

Growth of PQD: Cesium lead bromide perovskites (CsPbBr3) were synthesized by following the methods introduced by Protesescu et al.[35,50] In this method, 40 mL of ODE, and 700 mg of PbBr2 were synthesized by following the methods introduced by Protesescu et al. In this method, 40 mL of ODE, and 700 mg of PbBr2 were synthesized by following the methods introduced by Protesescu et al.

Sample Preparation: Large area monolayer MoS2 was grown using a promoter-assisted method via CVD.[10] As-grown MoS2 film on silicon wafer was spin-coated with PMMA C4 at 3000 rpm for 60 s. The sample was subsequently dried in an oven (80 °C) for 5 min and floated on a deionized water on a Petri dish. The PMMA/MoS2 film floating on water was rinsed thrice and transferred onto quartz and SiO2/Si substrates. The PMMA film was subsequently washed with acetone, isopropanol alcohol, and ethanol solution followed by annealing the sample at 350 °C under Ar/H2 environment to completely remove the organic contaminations on the MoS2 film. For the electrical and hall measurement, the samples transferred onto SiO2/Si were patterned by photolithography process for etching and electrode deposition followed by Cr/Au (10/50 nm) deposition using electron-beam evaporator at high vacuum. Similarly for the STM/S measurements, MoS2 films were transferred onto p-doped Si after removing the SiO2 layer by hydrofluoric acid treatment. As-prepared PQD on hexane was spin coated at 1000 rpm for 1 min in all MoS2 films under different substrates. The sample was then dried in vacuum desiccator for 24 h.

Characterization: The linear absorption of the pristine and heterostructure samples was analyzed using the Jasco V-670 spectrophotometer. Confocal absorption spectra imaging using a lab-made laser confocal microscopy system with a tungsten-halogen lamp was used to obtain absorption mapping and local spectra at a resolution of 1 µm diameter, detected by spectrometer. Raman, PL, and TRPL spectra were obtained under ambient conditions using a commercial multifunctional optical microscopy system (NT MDT, NTEGRA Spectra PNL) using two different excitation source of 2.331 eV (532 nm) and 3.062 eV (405 nm). The spatial resolution of the system was indicated to be 380 nm with an objective lens having numerical aperture of 0.7. TRPL measurement was set up with a time-correlated single photon counting system with a 3.062 eV (405 nm) pulsed laser with a repetition rate of 50 MHz and an pulse width down to 60 ps. Hall bar measurements were performed in a physical property measurement system (Quantum Design Inc.) coupled with the Agilent B1500A semiconductor device analyzer. TA measurements were performed using a 1 kHz Ti: sapphire regenerative amplifier (Libra, Coherent) operating at 790 nm which was divided into two beams. One operates an optical parametric amplifiers (TOPAS prime, Coherent) generating ultraviolet to mid-infrared range of laser light, which was used as a tunable pump pulse from visible to NIR (1.24–3.1 eV) with a pulse duration of 200 fs. The other was focused onto a nonlinear crystal to generate a white light continuum and used as a probe pulse that was detected by using a 256-pixel InGaAs sensor (HELIOS, Ultrafast systems). Photocurrent measurements were conducted at high vacuum (10⁻⁶ Torr) with a Keithley (4200-SCS) parameter analyzer in the dark and laser illumination condition. STM/S measurements were conducted for pristine and PQD/MoS2 heterostructure at room temperature using Omnicron VT-STM. Prior to STM measurements, both MoS2/Si, and PQD/MoS2/Si were cleaned in a UVH chamber with a base pressure <1.0 x 10⁻¹⁰ T by heating them at <100 °C for 2 h. Electrochemically etched W tips were used after electron bombardment to remove the surface oxide and contaminants. The dI/dV spectra were recorded by using a lock-in amplifier with a modulation voltage of 50 mV at 919 Hz. All the optical and electrical measurements were carried out by calibrating the instruments with standard references. For the instrument calibration and fitting of absorption and PL spectra, Gauss and Lorentz function were used within an accuracy of 15% error. The error bars in the optical and electrical measurements represent the errors estimated from the fitting or from data averaging process.

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

Acknowledgements
This work was supported by the Institute for Basic Science (IBS, R011-D1).

Conflict of Interest
The authors declare no conflict of interest.

Keywords
bandgap renormalization, charge transfer, CsPbBr3, quantum dots, MoS2 monolayers, room temperature

Received: May 12, 2020
Revised: August 2, 2020
Published online: September 21, 2020

[1] M. Kang, B. Kim, S. H. Ryu, S. W. Jung, J. Kim, L. Moreschini, C. Joziwiaik, E. Rotenberg, A. Bostwick, K. S. Kim, Nano Lett. 2017, 17, 1610.
[2] B. Scharf, T. Frank, M. Gmitra, J. Fabian, I. Žutić, V. Perebeinos, Phys. Rev. B 2016, 94, 245434.
[3] J. G. Roch, N. Leisgang, G. Froehlich, P. Makk, K. Watanabe, T. Taniguchi, C. Schönberger, R. J. Warburton, Nano Lett. 2018, 18, 1070.
[4] J. Klein, J. Wierzbowski, A. Regler, J. Becker, F. Heimbach, K. Müller, M. Kaniber, J. J. Finley, Nano Lett. 2016, 16, 1554.
[5] D. Y. Qiu, F. H. da Jornada, S. G. Louie, Phys. Rev. B 2016, 93, 235435.
[6] Y. Lin, X. Ling, L. Yu, S. Huang, A. L. Hsu, Y.-H. Lee, J. Kong, M. S. Dresselhaus, T. Palacios, Nano Lett. 2014, 14, 5569.
[7] A. Steinhoff, M. Rösner, F. Jahnke, T. O. Wehling, C. Gies, Nano Lett. 2014, 14, 3743.
[8] J. Ryu, Y.-S. Kim, S. Ke, K. Cho, Sci. Rep. 2016, 6, 29184.
[9] E. A. Apogna, M. Marsili, D. De Fazio, S. Dal Conte, M. Manzon, D. Sangalli, D. Yoon, A. Lombardo, A. C. Ferrari, A. Marini, G. Cerullo, D. Prezzi, ACS Nano 2016, 10, 1182.
[10] Y. Park, S. W. Han, C. S. Ch. Chan, B. P. L. Reid, R. A. Taylor, N. Kim, Y. Jo, H. Im, K. S. Kim, Nanoscale 2017, 9, 10647.
[11] S. Ulstrup, A. G. Cabo, J. A. Miwa, J. M. Riley, S. S. Granberg, J. C. Johannsen, C. Cacho, O. Alexander, R. T. Chapman, E. Springate, M. Bianchi, M. Dendzik, J. V. Lauritsen, P. D. C. King, P. Hofmann, ACS Nano 2016, 10, 6315.
[12] A. Walsh, J. L. F. Da Silva, S.-H. Wei, Phys. Rev. B 2008, 78, 075211.
