Metallic phase transition metal dichalcogenide quantum dots showing different optical charge excitation and decay pathways

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Abstract
The charge excitation and decay pathways of two-dimensional heteroatomic quantum dots (QDs) are affected by the quantum confinement effect, bandgap structure and strong exciton binding energy. Recently, semiconducting transition metal dichalcogenides (TMDs) have been intensively studied; however, the charge dynamics of metallic phase QDs (mQDs) of TMDs remain relatively unknown. Herein, we investigate the photophysical properties of TMD-mQDs of two sizes, where the TMD-mQDs show different charge excitation and decay pathways that are mainly ascribed to the defect states and valence band splitting, resulting in a large Stokes shift and two excitation bands for maximum photoluminescence (PL). Interestingly, the dominant excitation band redshifts as the size increases, and the time-resolved PL peak redshifts at an excitation wavelength of 266 nm in the smaller QDs. Additionally, the lifetime is shortened in the larger QDs. From the structural and theoretical analysis, we discuss that the charge decay pathway in the smaller QDs is predominantly affected by edge oxidation, whereas the vacancies play an important role in the larger QDs.

Introduction
Following extensive studies on two-dimensional (2D) layered materials, transition metal dichalcogenide (TMD)-based quantum dots (QDs) have attracted significant attention owing to their potential applications in optoelectronics, catalysis, biosensors, energy systems, etc1−4. The different structural phases, i.e., semiconducting (2H) and metallic (1T/1T′) phases, of 2D TMDs with stoichiometric combinations (MX2) of transition metals (M = Mo, W, Ni, etc.) and chalcogens (X = S, Se, Te) exhibit various electronic and optical properties5−8. The electronic and optical properties of TMD-QDs are usually explained by the combined mechanism of the quantum confinement effect, surface state, and doping effect9−11, which is also sensitive to environmental conditions, chalcogen defects, and heteroatomic crystal structures4,12,13. As the QDs form a monolayer, the electronic band structure widens to ~3−5 eV, with slight variations depending on the type of transition metal and chalcogen13,14. Furthermore, TMD-QDs exhibit a strong exciton binding energy and significantly enhanced spin-valley coupling, which induces broadening of excitonic absorption peaks and generates a higher quantum yield compared to the flake types2−4. MoSe2- and WS2-QDs show an excitation wavelength-dependent photoluminescence (PL) shift, suggesting two different recombination pathways of excitons15,16. However, to date, the optical properties of metallic phase TMD-QDs (TMD-mQDs) compared to those of semiconducting TMD-QDs have been ambiguous and not consistently reported4,17−19.

The spectroscopic results for metallic TMDs show additional Raman modes below 200 cm−1, a monotonic
change in UV-visible absorption, and a shift in photoelectron peaks \cite{6,20,21}. TMD-\textit{m}QDs that are electrochemically, hydrothermally, or mechanically fabricated in situ with a structural phase transition have distinctive advantages, such as high charge transfer and efficient catalytic properties \cite{4,22}. However, although the photophysical properties of metallic TMD-QDs are expected to be advantageous, most studies have focused on semiconducting TMD-QDs. This is mainly due to the various synthetic routes and particular phase engineering related to the metastable metallic phase of TMDs \cite{6,7,21,23,24}. Phase engineering for metallic phase TMDs has been developed via methods such as intercalation of alkali metals, electron-beam irradiation, and plasmonic hot electron injection, among others, including direct synthesis \cite{6,25,26}. Exfoliation by Li or K intercalation is the most preferred method for the synthesis of metallic phase TMDs \cite{5,7,21,20,24}, where high quality and phase stabilization are achieved simultaneously. Moreover, the phase stability is enhanced by lithiation, doping, vacancy defects, and lattice strain \cite{7,21,27,28}.

In this study, we report an in-depth investigation of the photophysical properties of metallic phase (1T//1T’\textsuperscript{\textdagger}) TMD (MX\textsubscript{2}, M = Mo, W; X = S, Se)-QDs synthesized using the K and Na intercalation method, in which the TMD-\textit{m}QDs were separated into two groups of different sizes (\textit{m}QDs-I: \textasciitilde3 nm, \textit{m}QDs-II: \textasciitilde12 nm). The metallic phase and structural properties were confirmed by high-resolution transmission electron microscopy (HR-TEM) showing an octahedral crystalline structure, novel Raman vibrational modes below 200 cm\textsuperscript{\textdagger}, and redshifted X-ray photoelectron spectroscopy (XPS) spectra. For the photophysical properties, various spectroscopic methods were employed, including excitation-dependent PL (PLE) with two resonance excitation bands and peak shifted time-resolved PL (TRPL) spectroscopy. Density functional theory (DFT) calculations revealed that the oxidation defects at the edge structure and vacancies on the basal plane play a role in controlling the electronic structure and exciton dynamics. Based on these analyses, a photo-electronic model of TMD-\textit{m}QDs is suggested.

**Results**

**Synthesis and characterization**

For years, we have developed the process of co-intercalation and exfoliation of TMDs using alkali metal-organic compounds, such as potassium sodium tartrate tetrahydrate salt, as shown in Fig. 1 (see details in the Experimental section and Supplementary Information)\textsuperscript{5}. In this study, we adopt this method to synthesize metallic phase TMD (MoS\textsubscript{2}, MoSe\textsubscript{2}, WS\textsubscript{2}, WSe\textsubscript{2})-QDs. The as-prepared TMD-salt compounds were instantly dispersed in water and sonicated for a few minutes, followed by filtration and dialysis. During the sonication process, TMD-QDs were explosively synthesized. Atomic force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM) revealed that TMD-QDs separated into two groups have sizes of \textasciitilde3 nm (QDs-I) and \textasciitilde12 nm (QDs-II; Fig. 2a). The AFM measurement yielded a QD thickness of 1–2 nm, regardless of the lateral size, implying that most QDs are mono- or bilayers (Supplementary Fig. S1). Figure 2b shows digital photographs of QDs-I and QDs-II dispersed in water at a concentration of 0.1 mg/ml, where QDs-I are significantly brighter and closer to the blue color compared to QDs-II under UV illumination. The dispersion stability is longer than 1 month, which is attributed to the partially negatively charged QDs, as examined by the zeta potential (Supplementary Fig. S2). Furthermore, HRTEM images directly demonstrate the lateral size and circular structure of the QDs (Fig. 2c and Supplementary Fig. S3). The analysis of magnified HRTEM images (inset of Fig. 2c) shows that the lattice constants of the (100) plane are 0.25, 0.23, 0.2, and 0.24 nm for MoS\textsubscript{2}, MoSe\textsubscript{2}, WS\textsubscript{2}, and WSe\textsubscript{2}, respectively, which are slightly smaller than those reported for 2H semiconducting TMD layers \cite{11,18,24,29}. The HRTEM image of QD-II shows point defects on the basal plane that are most likely related to chalcogen or metal atom vacancies (Fig. 2d, top)\textsuperscript{1,30}. The corresponding fast Fourier transform pattern demonstrates the octahedral crystalline structure of QDs typically observed in metallic phase TMDs (Fig. 2d, bottom). The metallic
phase of the QDs is also complemented by Raman and XPS spectra (Fig. 2e, f and Supplementary Fig. S4a, b). Novel vibrational modes assigned to $J_1$ (146.5 cm$^{-1}$), $J_2$ (235 cm$^{-1}$), and $J_3$ (335.5 cm$^{-1}$) bands appear in both Raman spectra of MoS$_2$ QDs-I and QDs-II, which are indicative of the distinct Raman signature of metallic phase MoS$_2$ (Fig. 2e)$^7,31$. Additionally, WSe$_2$ QDs show distinct vibrational modes below 225 cm$^{-1}$ related to the $J_1$, $J_2$, and $J_3$ transitions, while the absence of a $B_{2g}$ peak at 304 cm$^{-1}$ indicates a single layer similar to WSe$_2$ nanosheets (Fig. 2f)$^{24}$. With the similar tendencies in all WS$_2$ and WSe$_2$-QDs$^{32,33}$, novel vibrational modes below 200 cm$^{-1}$ are noted, suggesting that the as-prepared TMD-QDs are in the metallic phase (Fig. S4a, b). In the XPS spectra of Mo (Fig. 2g and Fig. S4c), the Mo3d$_{5/2}$ peak is shifted ~1 eV lower compared to that measured from 2H semiconducting MoX$_2$. In addition, separated W4f peaks clearly appear in the W spectra (Fig. 2h), and the assigned 1T W4f$_{5/2}$ peak is ~1 eV lower than the 2H W4f$_{5/2}$ peak (Fig. S4d). However, the characteristic in-plane ($E_{2g}^1$) and/or out-of-plane ($A_{1g}$) vibrational modes in the Raman spectra and the peak shift of the metal atom to a lower binding energy in the XPS spectra indicate that the as-prepared TMD-QDs could contain some portion of the polymorph structure, although the metallic phases (1T/1T$'$) are still dominant.

**Electronic and optical properties**

The as-prepared TMD-mQDs-I and -mQDs-II were investigated by UV-visible (UV-vis) absorbance and PLE (i.e., excitation wavelength ($\lambda_{Ex}$)-dependent emission wavelength ($\lambda_{Em}$)) measurements to determine their
electronic and optical properties (Fig. 3). Figure 3a clearly shows monotonically decreasing UV-vis absorbance spectra in both $m$QDs-I (left) and $m$QDs-II (right), indicating the metallic properties of the QDs. The Tauc plot applied for the direct transition bandgap ($E_{\text{og}}$; inset of Fig. 3a) provides estimated values of $E_{\text{og}} = 4.14–4.20$ eV, except for MoSe$_2$, with values of ~3.85 eV in $m$QDs-I and 3.88–3.93 eV in $m$QDs-II, although there is a deviation depending on the stoichiometry of the TMDs. The $E_{\text{og}}$ values larger than those of bulk or single-layer TMDs are assigned to an excitonic feature of the $m$QDs reflecting a strong quantum confinement effect$^{2,11,13,16}$, whereas the difference between $m$QDs-I and $m$QDs-II originates from the size difference. Figure 3b shows the PL spectra of $m$QDs-I excited at $\lambda_{\text{Ex}} \sim 260$ nm, which was greater than $E_{\text{og}}$, and the $m$QDs-II were excited at 360 nm, which was slightly less than $E_{\text{og}}$. The insets in a are Tauc plots ($\alpha h\nu$ vs. $h\nu$) for the optical bandgap. c–f PLE intensity of $m$QDs-I and -II of MoS$_2$ (c, d) and WSe$_2$ (e, f), where the measured $\lambda_{\text{Em}}$ varies from 380 to 640 nm. The emission wavelength ($\lambda_{\text{Em}}$) was measured from 380 nm to 560 nm. g–j 2D contour plots of $\lambda_{\text{Ex}}$ vs. $\lambda_{\text{Em}}$ for Fig. 3c–f.

The mQDs-I were excited at $\lambda_{\text{Ex}} \sim 260$ nm, which was greater than $E_{\text{og}}$, and the mQDs-II were excited at 360 nm, which was slightly less than $E_{\text{og}}$. The insets in a are Tauc plots ($\alpha h\nu$ vs. $h\nu$) for the optical bandgap. c–f PLE intensity of mQDs-I and -II of MoS$_2$ (c, d) and WSe$_2$ (e, f), where the measured $\lambda_{\text{Em}}$ varies from 380 to 640 nm. The emission wavelength ($\lambda_{\text{Em}}$) was measured from 380 nm to 560 nm. g–j 2D contour plots of $\lambda_{\text{Ex}}$ vs. $\lambda_{\text{Em}}$ for Fig. 3c–f.

Fig. 3 Excitation wavelength-dependent emission wavelength. a, b UV absorbance (a) and PL spectra (b) of mQDs-I (left) and mQDs-II (right).
of the TMDs. This feature is consistently observed in $m$QDs-II, although the intensity peaks are broadened and move to the longer wavelength region (A-band: 260–285 nm, B-band: 310–390 nm; Fig. 3e, f and Supplementary Fig. S5c, d). Interestingly, in $m$QDs-I, the PL intensity peak in the A-band is higher than that in the B-band, whereas it is similar to or smaller than that in the B-band in $m$QDs-II. For example, in WSe$_2$ $m$QDs-II, the PL intensity in the A-band becomes like or smaller than that in the B-band (Fig. 3f). The two bands are certainly not related to the neutral free excitons or bound excitons of TMDs because of the monotonically decreasing UV absorption and single peak of the PL spectrum. This is probably due to the band splitting by strong spin-valley coupling and the quantum size effect because the $\Delta E$ between the two PLE peaks is $\approx$0.7–0.9 eV, which is like the valence band splitting in semiconducting TMD-QDs$^{18}$. To date, this feature has not been reported for semiconducting TMD-QDs, which will be discussed more later. Two-dimensional contour plots for the correlation between the excitation and emission wavelengths are shown in Fig. 3g–j and Supplementary Fig. S6e–h. Two regions of luminescence maximum intensity corresponding to the PLE spectra are evidently shown. The point of maximum intensity in $m$QDs-I oscillates slightly as $\lambda_{\text{Ex}}$ increases from 250 to 340 nm, although it is gradually redshifted as $\lambda_{\text{Ex}}$ increases beyond 300 nm, which is usually observed in QDs. In contrast, the oscillation propensity of $m$QDs-II is weakened, while the highest intensity area moves into the B-band region.

**Exciton dynamics**

To further investigate the exciton dynamics of the TMD-$m$QDs, TRPL measurements were performed at two $\lambda_{\text{Ex}}$. As shown in Fig. 4a, b, the TRPL spectra of WSe$_2$ $m$QDs-I at $\lambda_{\text{Ex}} = 266$ nm show that the PL peak gradually redshifts from $\approx$410 to $\approx$470 nm as the delay time increases, whereas in WSe$_2$ $m$QDs-II, the redshift of the PL peak is trivial even after a delay time of 30 ns. Quantitative analysis of the peak shift at $\lambda_{\text{Ex}} = 266$ nm reveals that while the peak of $m$QDs-I redshifts to above 200 meV, it is $<100$ meV in $m$QDs-II (Fig. 4e). In comparison, the peak shift of the TRPL spectra at $\lambda_{\text{Ex}} = 360$ nm in both $m$QDs-I and -II is much less than that in WSe$_2$ $m$QDs-I excited at $\lambda_{\text{Ex}} = 266$ nm (Fig. 4c, d). The TRPL peak shift at $\lambda_{\text{Ex}} = 360$ nm is $<100$ meV in both $m$QDs-I and -II (Fig. 4f). This feature is analogously observed in all other TMD-$m$QDs (Supplementary Fig. S7). This suggests that some excitons formed at $\lambda_{\text{Ex}} = 266$ nm on $m$QDs-I steadily transit to the lower energy states together with an emissive decay, whereas excitons formed at $\lambda_{\text{Ex}} = 360$ nm on $m$QDs-II are likely to predominantly decay at the occurring sites. This speculation is indirectly supported by the PL decay dynamics. Although all exciton decay profiles from $m$QDs-I and -II are best fitted by a multiexponential function, the profiles from $m$QDs-II are closer to the monoexponential decay line (Fig. 4g). The average PL lifetime of $m$QDs-I is $3.94 \pm 0.12$ ns at $\lambda_{\text{Em}} = 420$ nm, which is longer than the value of $2.98 \pm 0.11$ ns for $m$QDs-II at $\lambda_{\text{Em}} = 460$ nm (Fig. 4h and Supplementary Fig. S8). This indicates that the exciton decay dynamics are different between $m$QDs-I and -II, which can be ascribed to the different emission sites originating from different defects on the $m$QDs.

**Theoretical calculation**

To prove our speculation that the electronic structure is affected by defects on TMD-$m$QDs, first-principles calculations within the density functional theory (DFT) framework were performed on the representative structural model of MoS$_2$. Figure 5a shows the variation in the bandgap of MoS$_2$ $m$QDs without defects with the QD size, where the bandgap increases as the size decreases due to the quantum confinement effect. However, during the synthetic process, the formation of vacancy defects on the basal plane and oxidation of edge-exposed atoms are inevitable. Figure 5b schematically illustrates the chalcogen vacancy (top) and oxygen defect (bottom) of the MoS$_2$ structure. Structural defects are assumed based on XPS analysis (Supplementary Fig. S5). When considering such defects, the electronic bandgap of MoS$_2$ is narrower than that of the pristine structure (Fig. 5c). Unexpectedly, with the band structure calculations (Supplementary Fig. S9), the vacancy defect on the basal plane conspicuously leads to a bandgap narrowing up to 0.2–0.4 eV compared to that of pristine MoS$_2$, which is a significantly larger variation than that induced by oxygen defects on the edge structure ($<0.1$ eV)$^{37}$. Furthermore, the energy difference (0.2–0.3 eV) between them corresponds well to the difference ($\approx$0.3 eV) between the PL peaks of $m$QDs-I and $m$QDs-II (Fig. 3b).

**Discussion**

Herein, the photophysical properties of metallic phase TMD-QDs are reported by comparing $m$QDs-I (~3 nm) and $m$QDs-II (~12 nm) of two sizes. Based on the above results, a model for possible optical excitation and relaxation pathways in $m$QDs-I and $m$QDs-II is schematically illustrated in Fig. 6a, b. Because the $\Delta E$ ($\approx$0.8 eV) between two PLE excitation bands (Fig. 3e–f) corresponds well to that of valence band splitting in TMD-QDs$^{18}$, the system is assumed to be resonantly excited from the valence band splitting states to the conduction band (SI and higher energy states) and lower defect states. Due to the metallic phase of QDs, strongly coupled exciton-plasmon polaritons might occur$^{38}$, where the resonance frequency varies with the size of $m$QDs. This, along with the defect-induced anisotropic confined excitons$^{12}$, may
cause oscillation of the PLE intensity peak (Fig. 3g–j) and variation of the relative quantum efficiency in mQDs-I and mQDs-II after considering UV absorption (Supplementary Fig. S10). Additionally, as the edge oxidation of mQDs-I with a size comparable to the exciton Bohr radius has a dominant effect on the electronic structure (Fig. 6a), which is in contrast to mQDs-II mainly affected by vacancy defects (Fig. 6b), the radiative decay site of excitons is different from that in mQDs-II, which results in the difference in the energy (~0.3 eV) and lifetime (~1 ns) of PL. This is supported by structural analysis (Fig. 2 and Supplementary Figs. S3–5) and theoretical DFT calculations (Fig. 5). In addition, the vacancy and edge oxidation defects inducing substantial electron density localization cause a large Stokes shift (Fig. 3b)\(^3\). In summary, the electronic and optical properties of metallic phase TMD-QDs (mQDs) revealed that the exciton quantum dynamics are affected by the quantum confinement effect, band splitting due to strong spin-valley coupling, and defects. Two resonance excitation bands and oscillation of the PLE intensity peak of TMD-mQDs are first reported, which have not yet been reported in semiconducting TMD-QDs. When the size of mQDs is close to the exciton Bohr radius, edge oxidation has a dominant effect on the electronic structure; however, if the size is sufficiently larger than the exciton Bohr radius, then the vacancy on the basal plane acts as the main site determining the electronic structure and exciton dynamics. Our findings expand the general understanding of the nonlinear photophysics of two-dimensional heteroatomic structured QDs, which is essential for the potential applications of excitons-plasmons induced by light-matter interactions in optoelectronics and bio-optoelectronics.

**Materials and methods**

**Metallic phase TMD-QDs**

Potassium sodium tartrate was used to intercalate Li and K into the TMDs at low temperature. The metal-intercalated compounds of TMDs were reacted in the autoclave vessel at 250 °C for 12 h and then instantly exfoliated in water with sonication. The synthesized mQDs were separated into two sizes through filtration and dialysis\(^5\).

**Characterization**

The morphology of mQDs was analyzed using AFM (SPA400, SII, Japan) in tapping mode under ambient conditions. UV/Vis spectra (UV-3101PC spectrometer), fluorescence spectra (Perkin-Elmer LS 55 luminescence spectrometer), XPS (Sigma Probe, AlKα), and transmission electron microscopy (TEM, Tiatan cubed G2 60-300) analyses were conducted. Raman spectra were obtained from 100 to 500 cm\(^{-1}\) using a Raman spectrometer (LabRAM HR...
Fig. 5 Theoretical calculation. a Bandgap expansion as a function of the lateral size of mQDs. b Schematic illustration of the oxidation defect (bottom) and chalcogen vacancy (top). c Band structure of MoS$_2$ with vacancy defects (left) and oxygen defects (right).

Fig. 6 Model for photophysical properties. Energy band diagram combined with UV absorption, PLE, and PL spectra of mQDs-I (a) and mQDs-II (b).
UV/Vis/NIR, excitation at 514 nm). PL measurements were carried out using a 325-nm He-Cd continuous-wave laser, monochromatic light from a 300W Xenon lamp, and UV spectrometers (Maya2000, Ocean Optics, USA) as a PL detector at room temperature.

Density functional calculations
DFT calculations were performed using the generalized gradient approximation (GGA) for the exchange-correlation potential and projector augmented wave potentials, as implemented in the VASP code. The wave functions were expanded in plane waves up to an energy cutoff of 400 eV. We employed a supercell geometry with a vacuum region of more than 8 Å to prohibit interactions between adjacent supercells (more details are given in the Supplementary Information).

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Author contributions
B.H.K., S.J., and S.-H.S. proposed and conducted the overall project, and M.H.J. and Y.-H.C. carried out the TRPL experiments. H.W.Y. and S.J. developed the synthetic process of MQDs. B.H.K. and S.-H.S. analyzed the data and composed the manuscript.

Data availability
The authors declare that all data supporting the findings of this study are available within the paper and its supplementary information file.

Conflict of interest
The authors declare no competing interests.

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