Supporting Information

Colloidal Single-Layer Quantum Dots with Lateral Confinement Effects on 2D Exciton
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2H WSe$_2$ multilayer quantum dots (MQDs)
The binding energies of W and Se of WSe$_2$ MQDs (i.e., W 4f$_{5/2}$ (34.4 eV), W 4f$_{7/2}$ (32.3 eV), Se 3d$_{3/2}$ (55.8 eV) and Se 3d$_{5/2}$ (54.9 eV)) measured using X-ray photoelectron spectroscopy (XPS) are consistent with the previously reported values of 2H WSe$_2$.

Figure S1. XPS spectra of WSe$_2$ MQDs. (a) W 4f and (b) Se 3d XPS spectra of WSe$_2$ MQDs.
Thickness measurement of WSe$_2$ single-layer quantum dots (SQDs) with various diameters

AFM images of the lateral size-controlled WSe$_2$ SQDs show that the thickness of each exfoliated quantum dot corresponds to the reported value of single-layer WSe$_2$. The height analysis of more than hundreds of WSe$_2$ SQDs shows that the average thickness is ~ 0.7 nm, which confirms that the produced nanoparticles are single layers.

**Figure S2.** AFM images and statistical analysis of the thickness profile of WSe$_2$ SQDs. AFM images of WSe$_2$ SQDs with a lateral size of (a) 2.5, (b) 5.8, and (c) 9.7 nm SQDs. (d) Histograms of thickness for WSe$_2$ SQDs with $d = 2.5$, 4.1, 5.8, and 9.7 nm, respectively.
**Time-resolved photoluminescence intensity measurement**

Fluorescence lifetime measurements were carried out using a PicoQuant Fluorescence lifetime system (PicoQuant Photonics North America Inc. Westfield, MA USA) equipped with a FluoTime 100 (Compact Fluorescence Lifetime spectrometer), and a PLS450 (sub-nanosecond pulsed LED, center wavelength: 460 nm) for measuring lifetimes of ensemble WSe$_2$ SQD solution. The acquired time dependent luminescence intensity data was fitted by multi-exponential function, $I(t)=\sum a_i \exp(-t/\tau_i)$, where $a_i$ and $\tau_i$ are the relative amplitude and time constant respectively. Two or three exponential functions were sufficient to fit the data. The averaged luminescence lifetime ($\tau=1/k$) was calculated as $(\sum a_i \tau_i)/((\sum a_i \tau_i^2)$. All fitting parameters are listed in table S1.

![Graph showing time-resolved photoluminescence intensity of WSe$_2$ QDs solution (red) and instrument response function (black).](image)

**Figure S3.** Time-resolved photoluminescence intensity of WSe$_2$ QDs solution (red) and instrument response function (black).

**Table S1.** Fitting curve of time dependent luminescence intensity data showed in figure S3. $a_i$ is the relative amplitude for $\tau_i$.

<table>
<thead>
<tr>
<th>$a_1$</th>
<th>$\tau_1$ (ns)</th>
<th>$a_2$</th>
<th>$\tau_2$ (ns)</th>
<th>$a_3$</th>
<th>$\tau_3$ (ns)</th>
<th>$\tau_{ave}$ (ns)</th>
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<tbody>
<tr>
<td>0.34</td>
<td>1.2</td>
<td>0.56</td>
<td>3.0</td>
<td>0.10</td>
<td>7.2</td>
<td>3.8</td>
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Excitation wavelength dependent PL measurement
The excitation wavelength dependent PL spectra of the colloidal solution of WSe$_2$ SQDs are obtained for excitation wavelengths of 320, 350, 370, and 405 nm. The PL peak shifts with the excitation wavelength due to the size heterogeneity of the ensemble sample, as a subset of WSe$_2$ SQDs is photo-selected at a given excitation wavelength. In contrast, the PL spectra of a single WSe$_2$ SQD exhibit identical PL spectra regardless of the excitation wavelengths.

Figure S4. PL measurement of WSe$_2$ SQDs. (a) Excitation wavelength dependent PL of the WSe$_2$ SQDs solution. (b) Excitation wavelength independent PL of a single WSe$_2$ SQD (Figure 4c). The PL spectra are normalized for easier comparison of the peak positions.

Table S2. Stokes shift and full width at half maximum (fwhm) of single-layer WSe$_2$ sheets and WSe$_2$ SQDs

<table>
<thead>
<tr>
<th></th>
<th>PL (eV)</th>
<th>Stokes shift (eV)</th>
<th>FWHM (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-layer</td>
<td>1.63</td>
<td>0.03</td>
<td>0.09</td>
</tr>
<tr>
<td>sheets$^1$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SQD-4</td>
<td>2.21</td>
<td>0.14</td>
<td>0.20</td>
</tr>
<tr>
<td>SQD-3</td>
<td>2.47</td>
<td>0.35</td>
<td>0.31</td>
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<td>SQD-2</td>
<td>2.79</td>
<td>0.44</td>
<td>0.44</td>
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<td>SQD-1</td>
<td>2.85</td>
<td>0.43</td>
<td>0.52</td>
</tr>
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**Linear polarization anisotropy measurement of the ensemble WSe$_2$ SQD film**

The linear PL polarization anisotropy of the WSe$_2$ SQD film is measured using far-field excitation (Figure S4a). A sample is prepared by drop-casting the SQD solution onto a sapphire window. A 405 nm laser light is used as the excitation source. Initially, the linearly polarized 405 nm beam is passed through a quarter waveplate to generate circularly polarized light. Subsequently, a linear polarizer is used to vary the linear polarization angle of the excitation light that impinges on the sample at a constant excitation intensity. The PL from the sample is collimated with an achromatic doublet lens, and its polarization is analyzed with a polarizer. The PL spectra are recorded with a CCD spectrometer (QE 65, Ocean Optics) after filtering out the excitation light using a long pass filter.

![Figure S5](image)

**Figure S5.** Linear polarization anisotropy measurement. (a) Schematic illustration of polarization anisotropy measurement of an ensemble film sample using linearly polarized far-field excitation. (b) Polar plot of the integrated PL intensity from the ensemble WSe$_2$ SQD film vs emission polarization angle for the excitation polarization angles of 0°, 45° and 90°. (c) Orientational correlation between excitation polarization angle ($\theta_{ex}$) and emission polarization angle ($\theta_{em}$). (d) PL polarization anisotropy ($r$) at three different $\theta_{ex}$. 
Circular polarization anisotropy measurement of the ensemble WSe\textsubscript{2} SQD film
The film sample is prepared by drop-casting the solution of WSe\textsubscript{2} SQDs on a sapphire window. The film on the sapphire window is mounted on an optical cryostat to perform the measurement at 10 K. A 405 nm laser is used as the excitation light source. The circularly polarized excitation light at 405 nm was generated by passing the linearly polarized 405 nm beam through a quarter waveplate. The helicity of the circular excitation is set at $\sigma^+$. The emission polarization of $\sigma^-$ or $\sigma^+$ is analyzed by a pair of a quarter waveplate and a linear polarizer. The PL spectra are recorded with a CCD spectrometer (QE65, Ocean Optics).

Figure S6. Circular polarization anisotropy measurement. Schematic of the circular polarization anisotropy measurement of the ensemble film sample.
Note S1. Effective mass approximation

The bandgap ($E_g$) of a semiconductor increases when its size approaches the exciton Bohr radius. We model a WSe$_2$ SQD as a cylindrical well with infinite barrier potential. According to the effective-mass approximation, the size dependence of the bandgap can be derived by the following equation:$^{2,3}$

$$E(a) = E_g + \frac{\hbar^2}{2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) \left( \frac{r_{nm}}{a} \right)^2$$

where $E_g$ is 1.66 eV, the direct band gap of monolayer WSe$_2$ nanosheets$^1$; $\hbar$ is Planck’s constant; $m_e$ is the effective mass of an electron in a WSe$_2$ in-plane lattice, 0.26 $m_o$; $m_h$ is the effective mass of a hole in the WSe$_2$ in-plane lattice, 0.33 $m_o$, with $m_o$ being the free-electron mass$^4$; $a$ is the radius; and $r_{nm}$ is the $n^{th}$ zero of the Bessel functions of order $m$. 
Note S2. Evanescent field intensity calculation

The vector components of the evanescent field \( (E) \) in the x, y, and z directions at the surface of the prism under total internal reflection are described by the following equation:

\[
E = A_x \cos \phi \exp[-i(\delta_P + \pi/2)] \hat{x} + A_y \sin \phi \exp(-i\delta_S) \hat{y} + A_z \cos \phi \exp(-i\delta_P) \hat{z}
\]

where \( \phi \) is the polarization angle of the incident linearly polarized light. \( A_x, A_y, A_z \) and the phase lags \( \delta_P \) and \( \delta_S \) depend on the incident angle of light at the prism surface and the refractive indices of the prism and its interfacial matrix.\(^5\) A WSe\(_2\) SQD is expected to possess an in-plane, 2D-isotropic absorption transition dipole; therefore, it should be excited only by the in-plane components of the evanescent field \((E_{\parallel})\). Because the PL intensity is proportional to the number of photons absorbed by the WSe\(_2\) SQD, \( E_{\parallel}^2 \) should exhibit a direct 1:1 correlation with the PL intensity.
References