Bright Monolayer Tungsten Disulfide via Exciton and Trion Chemical Modulations

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1. Optical properties

The photoluminescence (PL) spectra of monolayer WS$_2$ on SiO$_2$/Si substrate were conducted through a WITec alpha 300 R system with excitation wavelength of 532 nm at room temperature. In order to avoid heating and optical doping effect, the power of laser was kept as low as 7 $\mu$W for the room temperature PL measurement and 30 $\mu$W for the low temperature (77 K) circularly polarized PL measurement, respectively. The linear polarizer and quarter-wave plate were used for the measurement of circularly polarized PL spectra.

The pristine monolayer WS$_2$ shows a wide PL spectrum with an emission peak at ~1.99 eV, which is arising from both neutral exciton and electron bonded trion. In contrast, the PL spectra of the HATCN doped monolayer WS$_2$ become sharp and blue shift with an emission peak at ~2.02 eV, which is due to the transition from the trion to exciton through electron transfer from monolayer WS$_2$ to HATCN.

![Figure S1. Normalized PL spectra of pristine and HATCN doped monolayer WS$_2$.](image)
The non-uniformity intensity of the PL mapping may be due to the variation of natural doping (n doping) in pristine monolayer WS$_2$. The uneven distribution of natural doping could result in different formation possibility of electron bounded trion (low PL intensity) and neutral exciton (high PL intensity) in the different area of monolayer WS$_2$. As the PL spectrum of 1L-WS$_2$ is well reproduced by the sum of these two peak components, thus the different amount of trion and exciton would lead to different total intensity and position of the PL spectrum. As shown in supporting Figure 2, the PL spectrum extracted from the dark area (weak PL intensity) shows higher trion contribution (low energy PL shoulder) and red-shift compared to the spectrum extracted from the bright area, which should be due to its higher electron density than that of the bright area.

**Figure 2.** The PL spectra extracted from the bright (red) and dark (black) area of PL mapping (Inset).
Table S1. A brief summary of the PL enhancement in atomically thin transition-metal dichalcogenides (TMDCs).\cite{1-6}

<table>
<thead>
<tr>
<th>TMDCs</th>
<th>Dopant</th>
<th>PL enhancement factor$^a$</th>
<th>References</th>
</tr>
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<tr>
<td>WS$_2$</td>
<td>F4TCNQ</td>
<td>~2.3</td>
<td>S1</td>
</tr>
<tr>
<td>WS$_2$</td>
<td>fluorine plasma</td>
<td>~4.2</td>
<td>S2</td>
</tr>
<tr>
<td>WS$_2$</td>
<td>choline plasma</td>
<td>~3.0</td>
<td>S3</td>
</tr>
<tr>
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<td>F4TCNQ</td>
<td>~3.2</td>
<td>S4</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>TCNQ</td>
<td>~2.9</td>
<td>S4</td>
</tr>
<tr>
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<td>graphene</td>
<td>~2.0</td>
<td>S5</td>
</tr>
<tr>
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<td>gate voltage</td>
<td>~2.8</td>
<td>S6</td>
</tr>
<tr>
<td>WS$_2$</td>
<td>HATCN</td>
<td>~10</td>
<td>This work</td>
</tr>
</tbody>
</table>

$^a$The PL enhancement factor is defined as the ratio of the final integrated intensity of modified TMDCs to the integrated intensity of pristine TMDCs.
2. Raman spectra.

The Raman spectra of monolayer WS$_2$ on SiO$_2$/Si substrate were conducted through a WITec alpha 300 R system with excitation wavelength of 488 nm.

In order to exclude the strain and defect-induced PL enhancement, we measured the Raman spectra before and after HATCN doping. As shown in Figure S3, the E$_{2g}^{1}$ peak at $\sim$355 cm$^{-1}$ which is very sensitive to the strain is unchanged, indicating that the strain induced PL enhancement is negligible. Additionally, no defect peak can be observed, which demonstrates that the defect has little influence on the PL enhancement. In contrast, the A$_{1g}$ peak at $\sim$417 cm$^{-1}$ that is very sensitive to the charge density is blue-shift, confirming again the decrease of electron density in monolayer WS$_2$ owing to the charge transfer from WS$_2$ to HATCN.$^{[1]}$

![Figure S3. Raman spectra of pristine and HATCN doped monolayer WS$_2$.](image-url)
3. The framework of the three-energy-levels

According to the rate equation model [4], the population of neutral excitons ($N_X$) and trion ($N_{X^-}$) can be expressed in Equation (S1) and (S2),

$$\frac{dN_X}{dt} = G - \left[ \Gamma_{ex} + k_{tr}(n) \right] N_X$$  \hspace{1cm} (S1)

$$\frac{dN_{X^-}}{dt} = k_{tr}(n) N_X - \Gamma_{tr} N_{X^-}$$  \hspace{1cm} (S2)

where $G$ is the population of excitons after optical excitation, $k_{tr}(n)$ is the generation rate of the trion from the neutral exciton after $n$-th doping step, $\Gamma_{ex}$ and $\Gamma_{tr}$ are the decay rate of neutral exciton and trion, respectively. The experimental values of $\Gamma_{ex}$ and $\Gamma_{tr}$ measured from transient absorption measurement are 0.002 and 0.02 ps$^{-1}$, respectively [7].

The solution of these equations can be written in Equations (4) and (5), respectively,

$$N_X(n) = \frac{G}{\Gamma_{ex} + k_{tr}(n)}$$  \hspace{1cm} (S3)

$$N_{X^-}(n) = \frac{k_{tr}(n)}{\Gamma_{tr}} \frac{G}{\Gamma_{ex} + k_{tr}(n)}$$  \hspace{1cm} (S4)

Under the assumption that the langmuir’s law is valid, $k_{tr}(n)$ can be determined as follows [4],

$$k_{tr}(n) = k_{tr}(0) \left( 1 - s \frac{\alpha n \sigma}{1 + \alpha n \sigma} \right)$$  \hspace{1cm} (S5)

where $\alpha$ represents a parameter that indicates the HATCN adsorption probability onto the WS$_2$, $n$ is the doping step, $\sigma$ is the concentration of HATCN, $k_{tr}(0)$ is the formation rate of pristine monolayer WS$_2$. The experimental value of $k_{tr}(0)$ obtained from transient absorption measurement is 0.5 ps$^{-1}$.

According to the previous report, the PL intensity of neutral exciton ($I_X$) and trion ($I_{X^-}$) is proportional to the exciton populations, which can be expressed by the following equations
\[ I_X(n) = \frac{AG\gamma_{ex}}{\Gamma_{ex} + k_{tr}(n)} \] \hspace{1cm} (S6)

\[ I_X(n) = \frac{k_{tr}(n) AG\gamma_{tr}}{\Gamma_{tr} \Gamma_{ex} + k_{tr}(n)} \] \hspace{1cm} (S7)

where A is coefficient, \( \gamma_{ex} \) and \( \gamma_{tr} \) are the radiative decay rate of the exciton and trion, respectively. In this calculation, the change of \( \gamma_{ex} \) and \( \gamma_{tr} \) are neglected with doping for simplicity.
4. Mass action model

Under assuming that the mass action law is valid, the relationship among the population of neutral exciton, trion and electron density in monolayer WS$_2$ can be expressed as $^{[2]}$

$$\frac{N_X n_{el}}{N_{X^-}} = \left( \frac{4m_X m_e}{\pi \hbar^2 m_{X^-}} \right) k_B T \exp \left( \frac{E_b}{k_B T} \right)$$

(S8)

where $\hbar$ is the reduced Planck's constant, $k_B$ is the Boltzmann constant, $T$ is the temperature, $E_b$ (~26 meV) is the trion binding energy, $m_e$, $m_{X^-}$ and $m_X$ are electron, trion and exciton effective masses, respectively. $m_e$ and $m_h$ are 0.44$m_0$ and 0.45$m_0$, where $m_0$ is a free electron mass$^{[8]}$. The effective mass of a neutral exciton ($m_X$) and a trion ($m_{X^-}$) can be calculated as $m_X = m_e + m_h = 0.89m_0$, $m_{X^-} = 2m_e + m_h = 1.34m_0$, respectively$^{[2]}$.

With Equations S3, S4, S6, S7 and S8, the trion PL weight ($I_{X^-}/I_{total}$) can be determined as

$$\frac{I_{X^-}}{I_{total}} = \frac{\gamma_{tr} N_{X^-}}{\gamma_{ex} N_X} \approx \frac{1.65 \times 10^{-14} n_{el}}{1 + 1.65 \times 10^{-14} n_{el}}$$

(S9)

The Equation S9 could be used to calculate the electron density $n_{el}$ according to the experimental trion spectra weight.
5. Theoretical calculations

The theoretical calculations were conducted based on the Material Studio2017 Castep module with the GGA/PW91-OBS method.\cite{9} The Generalized Gradient Approximation (GGA) Perdew–Burke–Ernzerhof (PBE) \cite{10} method with Tkatchenko–Scheffler (TS) dispersion correction\cite{11} in CASTEP code with fixed the crystal lattice was used to optimize the geometry. The pseudopotentials are normconserving with a 500 eV energy cutoff. The max force is 0.02, and the max stress is 0.03 GPa, the k-points is $3 \times 3 \times 1$. The charge density difference was also calculated by GGA/PBE-TS method in VASP software with the PAW.

Table S2. The calculated charge transfer and absorption energy in chemical doped WS$_2$.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Charge transfer (e)</th>
<th>Absorption energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HATCN</td>
<td>-0.18</td>
<td>-1.93</td>
</tr>
<tr>
<td>F4TCNQ</td>
<td>-0.09</td>
<td>-1.28</td>
</tr>
</tbody>
</table>
6. Experimental Section

**Preparation and characterization of monolayer WS₂.** Bulk crystal WS₂ was purchased from HQ Graphene. The monolayer WS₂ flake was conveniently exfoliated from the commercial bulk crystals by the micromechanical method onto a Si wafer with a 280 nm thick SiO₂ capping layer. The optical image was taken by OLYMPUS BX51M. The AFM height image was recorded by Bruker, Dimension Edge.

**HATCN doping.** HATCN was purchased from HanShang Chemical Scientific Limited. HATCN was dissolved in toluene solution with the concentration of ~2×10⁻⁵ M. The dopant of HATCN was deposited via drop cast method. The volume of one step doping is ~ 10 μL. All of the measurements were performed after the sample dried in ambition condition.
References:


