Electrically Tunable and Dramatically Enhanced Valley-Polarized Emission of Monolayer WS$_2$ at Room Temperature with Plasmonic Archimedes Spiral Nanostructures

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Supporting Information

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Supporting Information 1.

We have characterized our single crystalline WS$_2$ samples using Raman spectroscopy and X-ray photoelectron spectroscopy (XPS), and the representative data are summarized below.

To demonstrate the crystallinity of single crystalline WS$_2$, we performed Raman spectroscopic studies of the $A_{1g}$ and $E_{2g}^1$ modes using a 514.3 nm laser (2.41 eV) as the excitation source, and a representative spectrum is shown in Figure S1.

![Figure S1. Raman spectrum of a monolayer WS$_2$, showing the $A_{1g}$ and $E_{2g}^1$ optical phonon modes, and the LA (M) mode associated with the longitudinal acoustic phonon at the M point of the Brillouin zone, which may be considered as an indicator of the sample quality.](image)

X-ray photoelectron spectroscopy (XPS) was also conducted to examine the chemical composition and valence states of monolayer WS$_2$ transferred to Au (111) / mica substrates. The core level spectra were calibrated via fitting adventitious carbon at 284.8 eV. The high-resolution spectra of W 4f and S 2p peaks are shown in Figure S2. For 2H-phase WS$_2$, the corresponding binding energies of the W 4f$_{7/2}$ and W 4f$_{5/2}$ peaks were found to locate at 32.15
and 34.31 eV, respectively, and the binding energies for the S 2p\(_{3/2}\) and S 2p\(_{1/2}\) peaks were located at 162.87 and 163.07 eV, respectively. These values are all consistent with those reported previously in literature.

**Figure S2.** XPS of a monolayer WS\(_2\), showing the W 4f\(_{7/2}\) and W 4f\(_{5/2}\) peaks in the left spectrum and the S 2p\(_{3/2}\) and S 2p\(_{1/2}\) peaks in the right spectrum.
Supporting Information 2.

The total decay rate of the as-grown monolayer WS\(_2\) without coupling to the plasmonic nanostructures is:

\[
\gamma_{\text{off}} = \gamma_R + \gamma_{\text{NR}},
\]

where \(\gamma_R\) and \(\gamma_{\text{NR}}\) are the radiative and nonradiative decay rates, respectively. The coupling to plasmonic nano-cavities enhances the radiative rate by the Purcell effect and induces a new decay channel through metallic losses with a rate \(\gamma_M\). Therefore, the total decay rate of the coupled monolayer WS\(_2\) can be expressed as:

\[
\gamma_{\text{on}} = (F_p + 1)\gamma_R + \gamma_{\text{NR}} + \gamma_M,
\]

where \(F_p\) is the Purcell factor that enhances the radiative decay rate. Therefore,

\[
\frac{\gamma_{\text{on}}}{\gamma_{\text{off}}} = \frac{(F_p + 1)\gamma_R + \gamma_{\text{NR}} + \gamma_M}{\gamma_R + \gamma_{\text{NR}}},
\]

In order to determine the underlying Purcell factor from the measured rates, we note that the quantum yield \(\eta\) is defined as the ratio of the number of photons emitted to the number of photons absorbed:

\[
\eta_{\text{off}} = \frac{\gamma_R}{\gamma_R + \gamma_{\text{NR}}},
\]

\[
\eta_{\text{on}} = \frac{(F_p + 1)\gamma_R}{\gamma_R + \gamma_{\text{NR}}},
\]

\[
\gamma_{\text{on}} - \gamma_{\text{off}} = F_p\gamma_R + \gamma_M.
\]

Therefore, the metallic-loss corrected Purcell factor \(F_p\) is given by:

\[
F_p = \left( \frac{F_p \gamma_R}{F_p \gamma_R + \gamma_M} \right) \left( \frac{\gamma_{\text{on}}}{\gamma_{\text{off}}} - 1 \right) \eta_{\text{off}}^{-1}.
\]
Figure S3. Time-resolved PL decay profile of a) WS$_2$ and b) WS$_2$-2TRHPAS.
Supporting Information 3.

Figure S4. Geometric structure and E-field distribution of WS$_2$-2TRHPAS heterostructure. a) SEM image of 2TRHPAS. (Scale bar: 1.25 μm). b) The spiral width, inner radius and pitch are 50 nm, 200 nm, and 310 nm, respectively. c) Near-field of $E_z$ in the x-y plane with a focusing spot under the RCP excitation. d) Near-field of $E_z$ in the x-y plane with focusing spot under LCP excitation. e) Phase map of $E_z$ in the x-y plane for RCP excitation. f) Phase map of $E_z$ in the x-y plane for LCP excitation.
Supporting Information 4.

Figure S5. Electric field (images) of WS$_2$ with a) 1-turn, b) 2-turn, c) 3-turn, and d) 4-turn RHPAS under RCP excitation. Focusing point at the center of the RHPAS structure can be obtained from 2- and 4-turn spirals. Corresponding phase distribution of WS$_2$ with e) 1-turn, f) 2-turn, g) 3-turn, and h) 4-turn RHPAS under RCP excitation.
Supporting Information 5.

Figure S6. a) – d) Circularly polarized emission from as-grown monolayer WS$_2$ with 1-turn PAS array under 514nm $\sigma^+$ excitation: a) $\sigma^+$ polarized emission and b) $\sigma^-$ polarized emission intensity mapping. c) A spatial map for the degree of valley polarization (DVP) in a WS$_2$ with 1-turn PAS array. d) Representative $\sigma^+$ (red) and $\sigma^-$ (blue) PL intensity spectra taken at room temperature on the WS$_2$ with 1-turn PAS array. e) – h) Monolayer WS$_2$ with 1-turn PAS array under 514nm $\sigma^-$ excitation: e) $\sigma^+$ polarized emission and f) $\sigma^-$ polarized emission intensity mapping. g) A spatial map for the degree of valley polarization (DVP) in a WS$_2$ with 1-turn PAS array. h) Representative $\sigma^+$ (navy) and $\sigma^-$ (orange) PL intensity spectra taken at room temperature on the WS$_2$ with 1-turn PAS array.
Figure S7. a) – d) Circularly polarized emission from as-grown monolayer WS$_2$ with 2-turn PAS array under 514nm $\sigma^+$ excitation: a) $\sigma^+$ polarized emission and b) $\sigma^-$ polarized emission intensity mapping. c) A spatial map for the degree of valley polarization (DVP) in a WS$_2$ with 2-turn PAS array. d) Representative $\sigma^+$ (red) and $\sigma^-$ (blue) PL intensity spectra taken at room temperature on the WS$_2$ with 2-turn PAS array. e) – h) Monolayer WS$_2$ with 2-turn PAS array under 514nm $\sigma^-$ excitation: e) $\sigma^+$ polarized emission and f) $\sigma^-$ polarized emission intensity mapping. g) A spatial map for the degree of valley polarization (DVP) in a WS$_2$ with 2-turn PAS array. h) Representative $\sigma^+$ (navy) and $\sigma^-$ (orange) PL intensity spectra taken at room temperature on the WS$_2$ with 2-turn PAS array.
Supporting Information 7.

**Figure S8.** a) – d) Circularly polarized emission from as-grown monolayer WS2 with 3-turn PAS array under 514nm $\sigma^+$ excitation: a) $\sigma^+$ polarized emission and b) $\sigma^-$ polarized emission intensity mapping. c) A spatial map for the degree of valley polarization (DVP) in a WS2 with 3-turn PAS array. d) Representative $\sigma^+$ (red) and $\sigma^-$ (blue) PL intensity spectra taken at room temperature on the WS2 with 3-turn PAS array. e) – h) Monolayer WS2 with 3-turn PAS array under 514nm $\sigma^-$ excitation: e) $\sigma^+$ polarized emission and f) $\sigma^-$ polarized emission intensity mapping. g) A spatial map for the degree of valley polarization (DVP) in a WS2 with 3-turn PAS array. h) Representative $\sigma^+$ (navy) and $\sigma^-$ (orange) PL intensity spectra taken at room temperature on the WS2 with 3-turn PAS array.
Figure S9. a) – d) Circularly polarized emission from as-grown monolayer WS2 with 4-turn PAS array under 514nm $\sigma^+$ excitation: a) $\sigma^+$ polarized emission and b) $\sigma^-$ polarized emission intensity mapping. c) A spatial map for the degree of valley polarization (DVP) in a WS2 with 4-turn PAS array. d) Representative $\sigma^+$ (red) and $\sigma^-$ (blue) PL intensity spectra taken at room temperature on the WS2 with 4-turn PAS array. e) – h) Monolayer WS2 with 4-turn PAS array under 514nm $\sigma^-$ excitation: e) $\sigma^+$ polarized emission and f) $\sigma^-$ polarized emission intensity mapping. g) A spatial map for the degree of valley polarization (DVP) in a WS2 with 4-turn PAS array. h) Representative $\sigma^+$ (navy) and $\sigma^-$ (orange) PL intensity spectra taken at room temperature on the WS2 with 4-turn PAS array.
Supporting Information 9.

To investigate the effect of the plasmonic Archimedes spiral (PAS) resonance wavelength ($R_{\text{Plasmon}}$) on the enhancement of the DVP, we performed measurements of three different resonance wavelengths. The resonance wavelengths of the PAS nanostructures are $R_{\text{Plasmon}} = 310 \text{ nm} \ (2.42 \times 10^{14} \text{ Hz}), 620 \text{ nm} \ (4.84 \times 10^{14} \text{ Hz})$ and $930 \text{ nm} \ (7.26 \times 10^{14} \text{ Hz})$, respectively, and the corresponding photoluminescence (PL) spectra and the DVP values are shown in Figure S10 below. These studies suggest that the best room temperature DVP enhancement occurred when the resonance wavelength $R_{\text{Plasmon}}$ of the PAS nanostructures is 620 nm, which coincided with the neutral A-exciton emission wavelength.

![Diagram of PAS nanostructures with resonance wavelengths](image)

**Figure S10.** Schematics of the PAS nanostructures and the corresponding DVP. The spiral width and inner radius are 50 nm and 200 nm, respectively. The resonance wavelengths are a) 310 nm, b) 620 nm, and c) 930 nm, respectively. The corresponding $\sigma^+$ (red) and $\sigma^-$ (blue) PL intensity spectra were shown in d-f). g) Summary of the three different resonance wavelengths corresponding to the DVP, showing the best DVP for the resonance wavelength 620 nm that coincides with the A-exciton emission wavelength.
Supporting Information 10.

Figure S11. Gaussian–Lorentzian fitting of the electric tuning PL spectra of pure monolayer WS\textsubscript{2} under $V_{\text{Gate}} =$ a) 25 V, b) 20 V, c) 15 V, d) 10 V, e) 5 V, f) 0, g) $-5$ V, h) $-10$ V, i) $-15$ V, j) $-20$ V, and k) $-25$ V. Two spectral components, the A-exciton (yellow line), and trion (navy line), were obtained by the Gaussian–Lorentzian fitting.
Supporting Information 11.

Figure S12. Gaussian–Lorentzian Fitting of the electric tuning PL spectra of WS$_2$-2TRHPAS under $V_G =$ a) 25 V, b) 20 V, c) 15 V, d) 10 V, e) 5 V, f) 0, g) −5 V, h) −10 V, i) −15 V, j) −20 V, and k) −25 V. Two spectral components associated with the A-exciton (yellow line) and trion (navy line) were obtained by the Gaussian–Lorentzian fitting.
**Figure S13.** a) Contour plot of the PL spectra of 1L-WS₂ as a function of applied gate voltage (V₆₅₆) at RT. b) PL spectra at RT for V₆₅₆ from –25 V to 25 V, with an increment of 5 V. c) Gate voltage dependence of the PL peak position of neutral exciton (blue) and trion (red) under V₆₅₆ from –25 V to 25 V, together with the intensity ratio of trions and excitons (green) as a function of V₆₅₆ from –25 V to 25 V.
Figure S14. a) Contour plot of the PL spectra of 1L-WS$_2$ as a function of applied gate voltage ($V_{\text{Gate}}$) at RT. Polarization-resolved PL spectra under $\sigma^+$ (RCP) excitations for b) $V_{\text{Gate}} = 5$ V and c) $V_{\text{Gate}} = -2$ V.
Supporting Information 14.

**Figure S15.** Electric tuning of circularly polarized emission from monolayer (1L) WS$_2$ with 2-turn right-handed (RH) PAS array under 514 nm $\sigma^+$ excitation. a) $\sigma^+$ polarized emission and b) $\sigma^-$ polarized emission intensity mapping under $V_{\text{Gate}} = -20$ V. c) A spatial map for the degree of valley polarization (DVP) in a 1L-WS$_2$ with 2TRHPAS array under $V_{\text{Gate}} = -20$ V. d) Representative $\sigma^+$ (red) and $\sigma^-$ (blue) PL intensity spectra under $V_{\text{Gate}} = -20$ V taken at room temperature on the 1L-WS$_2$ with 2TRHPAS array.
Figure S16. Transfer characteristic curve ($I_{ds}$-$V_{gs}$) of a WS$_2$-2TRHPAS heterostructure FET measured at a source-drain voltage $V_{ds} = 0.1$ V.