SUPPORTING INFORMATION

Enhancement of Room Temperature Photoluminescence and Valley Polarization of Monolayer and Bilayer WS₂ via Chiral Plasmonic Coupling

Gaohong Liu[†], Xuanli Zheng[†], Haiyang Liu[†], Jun Yin[†], Congming Ke[†], Weihuang Yang[‡], Yaping Wu^{*,†}, Zhiming Wu^{*,†}, Xu Li[†], Chunmiao Zhang[†], and Junyong Kang[†] [†]Department of Physics, OSED, Fujian Provincial Key Laboratory of Semiconductor Materials and Applications, Xiamen University, Xiamen, 361005, P. R. China [‡]Key Laboratory of RF Circuits and System of Ministry of Education, Hangzhou Dianzi University, Hangzhou, 310018, P. R. China

*correspond to: ypwu@xmu.edu.cn, zmwu@xmu.edu.cn

S1. Schematic diagram for the preparation process of Au single- and dimer-prism arrays

Single-layer PS nanospheres are employed as the mask for constructing the Au single- and dimer-prism arrays.^{1,2} Figure S1a shows the preparation process of PS nanospheres arrays on a SiO₂/Si substrate using a self-assembly technology. First, the ultrasonically cleaned SiO₂/Si wafer is put into a quartz container which is immersed by deionized water. Then, the PS nanospheres with a diameter of 530 nm are diluted with alcohol, and are slowly injected onto the surface of the deionized water to form single-layer arrays with hexagonal-closed package. After evaporation of the deionized water, the PS nanosphere arrays are regularly arranged on the SiO₂/Si surface.

Using the PS nanospheres arrays as a mask, Au atoms are deposited onto the SiO₂/Si surface through conventional and angle-resolved lithography. Consequently, Au single- and dimer-arrays are obtained, as shown in Figure S1b, where θ represents the angle between the deposition direction³ and the normal direction of the mask in the angle-resolved lithography process.



Figure S1. Schematic diagrams of the preparation process of (a) the PS nanospheres arrays and (b) the Au single- and dimer-prism arrays.

S2. Optical images and 2D PL mapping

The morphologies of WS_2/Au heterostructures are observed through an optical microscope, as shown in Figure S2, where the areas with and without Au arrays beneath can be clearly distinguished. The corresponding PL mappings from the same areas confirm the uniformity of resonant enhancements, and further demonstrate the globally larger enhancement effect for Au (II) arrays than Au (I) arrays.



Figure S2. (a, b) Optical images of monolayer WS_2 (ML- WS_2) transferred on SiO₂/Si substrates with partly covering the Au (I) and Au (II) arrays, respectively. (c) Optical images of bilayer WS_2 (BL- WS_2) transferred on SiO₂/Si substrates with partly covering the Au (II) arrays. (d, e, f) The corresponding PL mappings of (a, b, c).

S3. Optical images, PL mapping, Single PL spectra and element distributions (EDS) mapping of WS₂/Al₂O₃/Au (II) system

In order to clarify the competitive relation between PL enhancement and fluorescence quenching effect, we perform the experiments to compare the PL enhancements with and without a 1.0 nm Al₂O₃ insulating layer between monolayer WS₂ and Au, as shown in Figure S3. Compared with pristine monolayer WS₂, the PL spectrum is uniformly enhanced in WS₂/Al₂O₃/Au (\mathbf{I}) system, displaying an 8.5 times enhancement, a little larger than the 7 times enhancement in WS₂/Au (\mathbf{I}) system. So, the enhancement effect is only slightly improved when adding the Al₂O₃ insulating layer. This indicates that, the quenching effect is suppressed. But simultaneously, owing to the increased distance between WS₂ and Au when adding the Al₂O₃ layer, the plasmonic coupling between WS₂ and Au may be weakened also. As a result, the PL enhancement is not intrinsically and obviously improved.



Figure S3. (a) Optical images of ML-WS₂/Al₂O₃/Au (\mathbb{I}). (b) The corresponding PL mapping of (a). (c) PL spectra of the ML-WS₂ taken in the areas without and with the Au (II) arrays beneath, respectively. (d-f) The SEM image of partly covered Au (II) arrays and the corresponding distribution of Au and Al elements.

S4. XPS spectra of as-grown monolayer WS₂

Stoichiometry and bonding states of as-grown monolayer WS₂ are characterized by XPS, as shown in Figure S4. The W signal illustrates three typical peaks at the binding energies of 33.43, 35.65, and 38.78 eV, corresponding to $4f_{7/2}$, $4f_{5/2}$, and $5p_{3/2}$ states, respectively. The S signal is composed of $2p_{3/2}$ and $2p_{1/2}$ peaks with the binding energies of 163.25 and 164.11 eV, respectively. The stoichiometric ratio of W: S is estimated to be 1: 2, which is consistent with the previously reported CVD-grown WS₂.⁴



Figure S4. XPS spectra of as-grown monolayer WS₂.

S5. Near-field intensity distribution of the monolayer and bilayer WS₂/Au hybrids under linearly polarized excitation



Figure S5. Near-field intensity distribution of (a, b) monolayer and (c, d) bilayer WS_2/Au heterostructures at 532 nm along the Au/SiO₂ interface (log scale). (a, c) and (b, d) correspond to the WS_2/Au single- and dimer-prism heterostructures, respectively.

S6. Near-field intensity distribution in monolayer WS₂/Au heterostructures under circularly polarized excitation



Figure S6. Near-field intensity distribution of monolayer WS_2/Au heterostructures at 532 nm under (a-d) LCP and (e-f) RCP excitation (log scale). (a, c, e, g) correspond to the cross-section at the WS_2/Au interface along the x-y plane, and (b, d, f, h) correspond to the cross-section on the black dashed along the x-z plane.

S7. Near-field intensity distribution in bilayer WS₂/Au heterostructures under circularly polarized excitation



Figure S7. Near-field intensity distribution of bilayer WS_2/Au heterostructures at 532 nm under LCP (a-d) and RCP (e-f) excitation (log scale). (a, c, e, g) correspond to the cross-section at the WS_2/Au interface along the x-y plane, and (b, d, f, h) correspond to the cross-section on the black dashed along the x-z plane.



S8. Near-field intensity distribution $E_{\rm L}$ and $E_{\rm R}$ in monolayer WS_2/Au heterostructures

Figure S8. Near-field intensity distribution (a-d) E_L and (e-h) E_R in monolayer WS₂/Au heterostructures, with LCP and RCP excitation at 532 nm (log scale).

S9. Time-resolved photoluminescence (TRPL) in bilayer WS_2/SiO_2 and bilayer WS_2/Au heterostructures



Figure S9. TRPL measurements in bilayer WS_2/SiO_2 , bilayer WS_2/Au (I) and bilayer WS_2/Au (II) heterostructures.

S10. Valley-polarized PL spectra of monolayer and bilayer WS₂ on SiO₂ and Au (II) arrays under a 589 nm resonant excitation at room temperature



Figure S10. (a, b) Valley-polarized PL spectra of monolayer WS_2 on SiO_2/Si and Au (II) arrays, respectively. (c, d) Valley-polarized PL spectra of bilayer WS_2 on SiO_2/Si and Au (II) arrays, respectively. The spectra are measured under a 589 nm resonant excitation at room temperature.

REFERENCES

- Haynes, C. L.; Van Duyne, R. P. Dichroic Optical Properties of Extended Nanostructures Fabricated using Angle-resolved Nanosphere Lithography. *Nano Lett.* 2003, *3*, 939-943.
- (2) Zhang, X. L.; Dai, Z. G.; Zhang, X. G.; Dong, S. L.; Wu, W.; Yang, S. K.; Xiao, X. H.; Jiang, C. Z. Recent Progress in the Fabrication of SERS Substrates Based on the Arrays of Polystyrene Nanospheres. *Sci. China-Phys. Mech. Astron.* 2016, *59*, 116801.
- (3) Cong, C. X.; Shang, J. Z.; Wang, Y. L.; Yu, T. Optical Properties of 2D Semiconductor WS₂. Adv. Opt. Mater. 2018, 6, 1700767.
- (4) Chen, J. J.; Shao, K.; Yang, W. H.; Tang, W. Q.; Zhou, J. P.; He, Q. M.; Wu, Y. P.; Zhang, C. M.; Li, X.; Yang, X.; Wu, Z. M.; Kang, J. Y. Synthesis of Wafer-Scale Monolayer WS₂ Crystals toward the Application in Integrated Electronic Devices. *ACS Appl. Mater. Interfaces* 2019, *11*, 19381-19387.