

Supporting Information

Mirror-Induced Electromagnetic Asymmetry Enables Greatly Enhanced Second-Harmonic Generation from 2H-Phase WS₂ Nanoparticles

Yeshun Guo, Chaomian Wu, Yuheng Mao, Jiancheng Xu, Shulei Li, Jingdong Chen, Lujun Huang, Fu Deng*, and Sheng Lan*

Mr. Yeshun Guo, Mr. Chaomian Wu, Mr. Yuheng Mao, Mr. Jiancheng Xu, Dr. Fu Deng, and Prof. Sheng Lan

Guangdong Provincial Key Laboratory of Nanophotonic Functional Materials and Devices,
School of Optoelectronic Science and Engineering, South China Normal University,
Guangzhou 510006, China

E-mail: dengfu@m.scnu.edu.cn (F. Deng)

Dr. Shulei Li

School of Physics and Optoelectronic Engineering, Guangdong Polytechnic Normal
University, Guangzhou 510665, China

Dr. Jingdong Chen

Key Laboratory of Light Field Manipulation and System Integration Applications in Fujian
Province, School of Physics and Information Engineering, Minnan Normal University,
Zhangzhou 363000, China

Prof. Lujun Huang

School of Physics, East China Normal University, Shanghai 200241, China

E-mail: ljhuang@phy.ecnu.edu.cn (L. Huang)

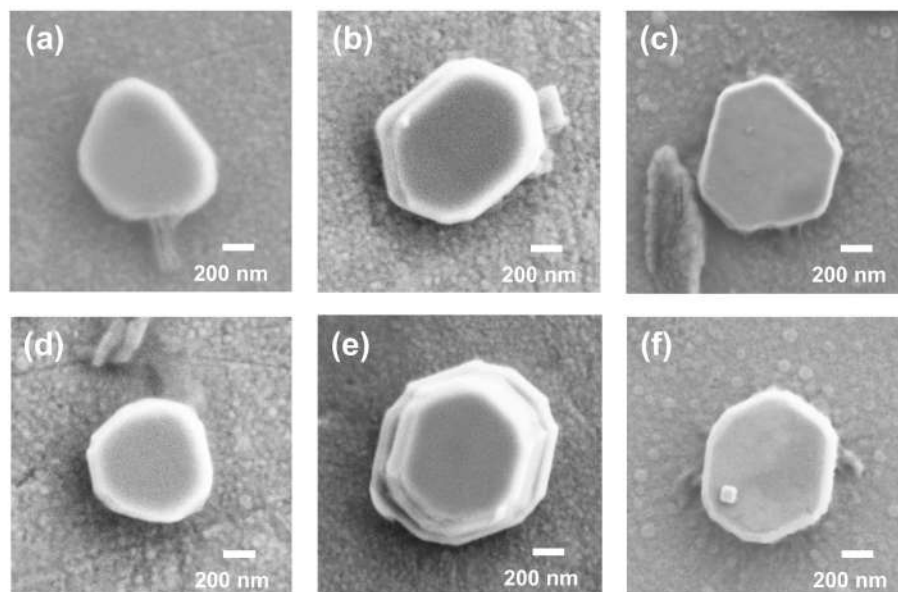
Supplementary Note 1. Representative SEM images of WS₂ nanoparticles on Ag film

Figure S1. Representative SEM images of WS₂ nanoparticles. (a–f) SEM images of representative isolated WS₂ nanoparticles dispersed on the SnO₂/Ag/SiO₂ substrate, illustrating particle-to-particle variations in lateral dimensions and edge morphology. The corresponding long-axis lengths L are approximately 842, 1001, 945, 748, 1145, and 826 nm for the nanoparticles shown in (a–f), respectively, spanning a range of approximately 748–1145 nm.

Supplementary Note 2. Size-dependent scattering spectra of WS₂ nanoparticles

Figure S2a presents the simulated scattering spectra of WS₂ nanoparticles supported on a SnO₂/Ag/SiO₂ substrate as a function of particle thickness, with the long-axis length fixed at $L = 1200$ nm. The red dashed line traces the spectral evolution of the ED-dominated nanoparticle–mirror hybrid resonance considered here, which moves progressively towards longer wavelengths as the particle thickness increases. This spectral shift can be attributed to the concomitant increase in the effective optical path length, which lowers the eigenfrequency of the corresponding hybrid mode. Under otherwise identical conditions, Figure S2b shows a similar redshift of the corresponding hybrid mode as the long-axis length is increased at a fixed particle thickness $h = 135$ nm, further demonstrating the size dependence of the resonance associated with SHG enhancement. Accordingly, the “Ag off-res.” condition used in the main text refers to a WS₂ nanoparticle on the same SnO₂/Ag/SiO₂ substrate whose hybrid resonance is spectrally shifted away from the excitation wavelength of 790 nm, rather than to the absence of an optical resonance.

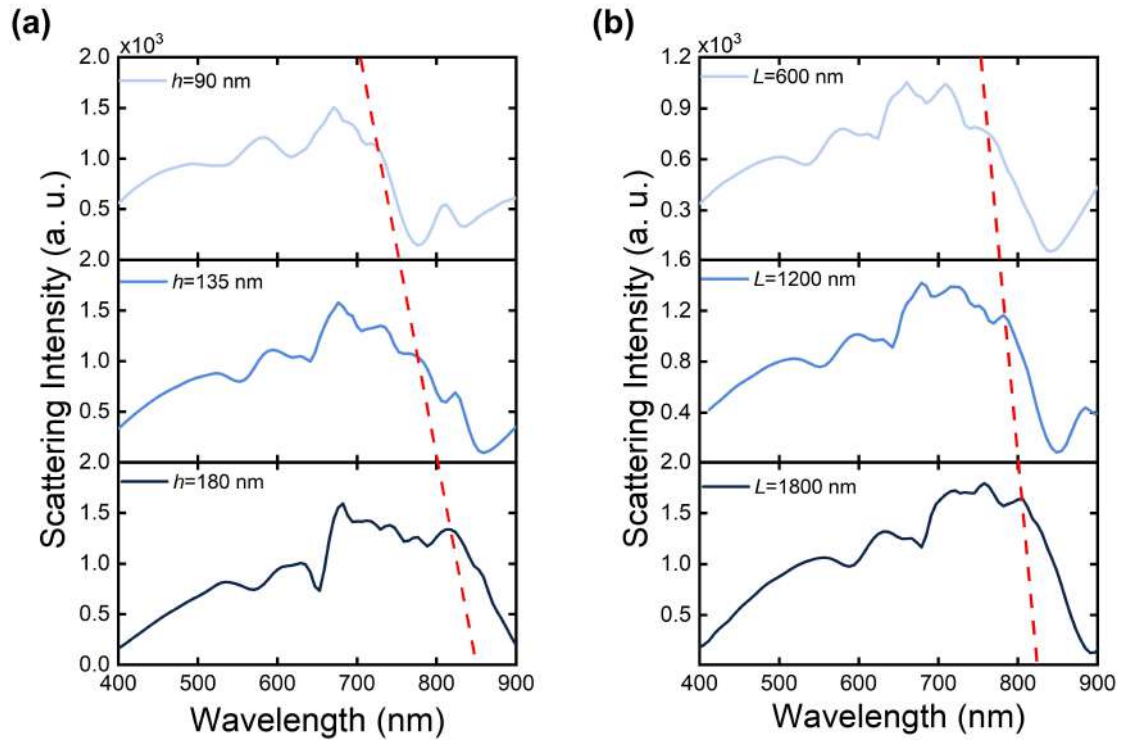
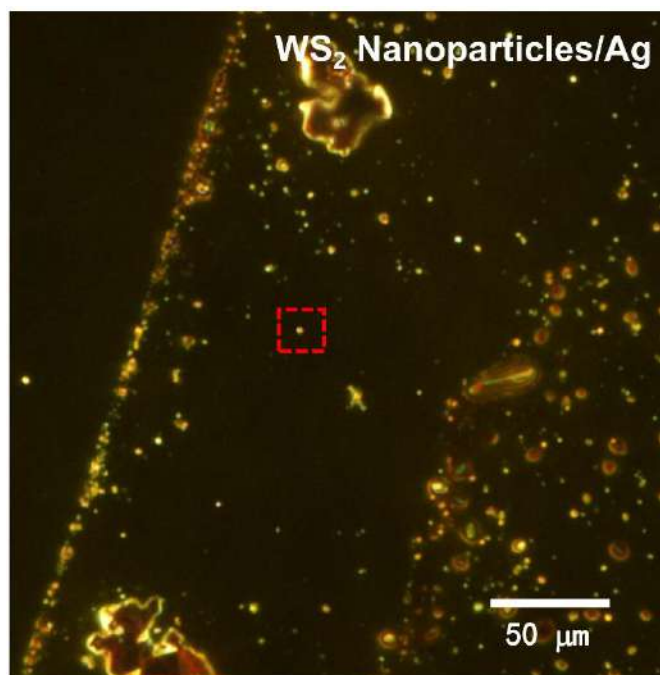


Figure S2. Simulated size-dependent scattering spectra of WS₂ nanoparticles on a SnO₂/Ag/SiO₂ substrate. (a) Scattering spectra calculated for different particle thicknesses h , with the long-axis length fixed at $L = 1200$ nm. (b) Scattering spectra calculated for different long-axis lengths L , with the particle thickness fixed at $h = 135$ nm. The red dashed lines trace the spectral evolution of the ED-dominated hybrid nanoparticle–mirror resonance.

Supplementary Note 3. Dark-field image of WS₂ nanoparticles on Ag film**Figure S3.** Dark-field optical image of WS₂ nanoparticles on SnO₂/Ag/SiO₂ substrate.

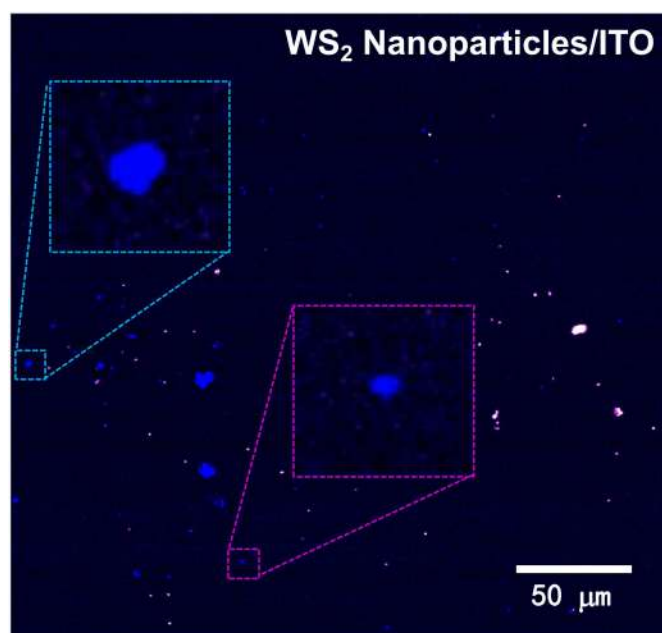
Supplementary Note 4. Scanning SHG image of WS₂ nanoparticles on ITO

Figure S4. Scanning SHG image of WS₂ nanoparticles on the ITO substrate.

Supplementary Note 5. Optical properties of bulk WS₂ for comparison

Figure S5a illustrates the scanning SHG image of bulk WS₂ flake (thickness larger than 1 μm) on the same SnO₂/Ag/SiO₂ substrate, where the SHG signal is mainly observed at the flake edges, consistent with surface- and edge-related nonlinear contributions. Confirming from the scattering spectrum of the bulk WS₂ flake (as shown in Figure S5b), only broaden spectrum causing from the reflection of the white light with visible exciton absorption around 630 nm. The spectrum is quite different from the scattering of WS₂ nanoparticle, which has pronounced optical resonance, as illustrated in the main text. To compare the nonlinear response of the bulk WS₂ flake with that of the WS₂ nanoparticles on the SnO₂/Ag/SiO₂ substrate, the excitation-power- and excitation-wavelength-dependent SHG spectra of the bulk flake are shown in Figures S5c and S5d. It is found that the SHG emission is much weaker than that of SHG from WS₂ nanoparticle on Ag film and the SHG spectra shows weak dependence on the excitation wavelength. These results are consistent with the centrosymmetric nature of bulk 2H-phase WS₂ and its correspondingly weak surface- and edge-related SHG response, while underscoring the roles of mirror-induced interfacial electromagnetic asymmetry and resonance-enhanced local-field confinement in the much stronger SHG observed from the WS₂ nanoparticles.

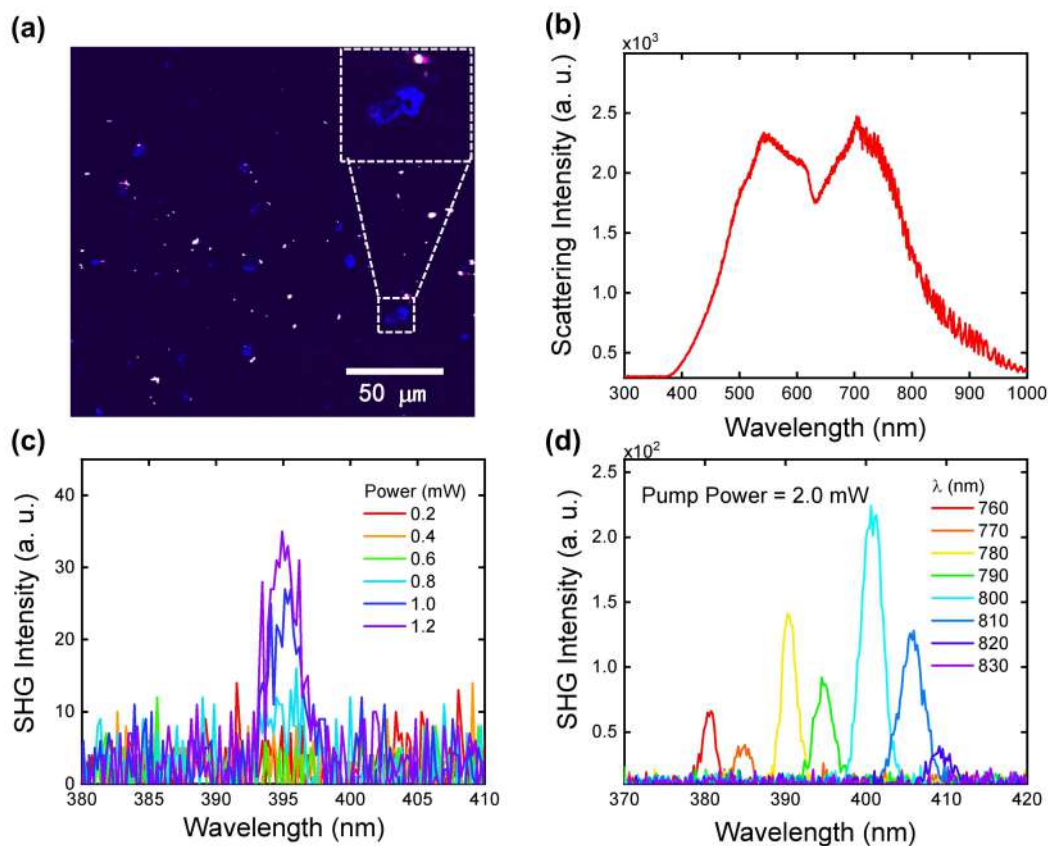


Figure S5. Optical properties of bulk WS₂. (a) Laser-scanning confocal microscopy images of SHG collected from bulk WS₂ flakes under a fixed excitation power of 1 mW. Enlarged views

of representative area are shown to highlight the spatial localization of the SHG emission. (b) Scattering spectrum of selected bulk WS₂ flake. (c) SHG spectra of the bulk WS₂ flake with varying excitation power at 790 nm. (d) Excitation wavelength dependent SHG spectra of the bulk WS₂ flake at excitation power of 2 mW.

Supplementary Note 6. Simulated electric-field intensity distributions under different conditions

For ideal bulk 2H-phase WS₂, the intrinsic crystal lattice is centrosymmetric, such that the electric-dipole (ED)-allowed second-order nonlinear response vanishes in the bulk under the ED approximation. When a WS₂ nanoparticle is placed on the SnO₂/Ag/SiO₂ substrate, however, the upper WS₂/air interface and the lower WS₂/SnO₂ interface become electromagnetically inequivalent owing to the presence of the underlying Ag mirror. The interaction between the nanoparticle and the metallic mirror produces strong fundamental-field localization near the lower interface and consequently establishes a pronounced top–bottom asymmetry in the local electromagnetic field. Such electromagnetic asymmetry can suppress the complete cancellation of nonlinear polarizations generated at the two interfaces, thereby enabling a finite second-order response.

As shown in Figure S6a, the electric-field intensity distributions in the x – y planes at the top ($h = 135$ nm) and bottom ($h = 0$ nm) surfaces reveal a substantial difference between the upper and lower surfaces of the WS₂ nanoparticle. The corresponding z -dependent intensity profile extracted along the vertical yellow dashed line further demonstrates a pronounced spatial variation in the fundamental field across the nanoparticle thickness. This top–bottom electromagnetic inequivalence can suppress the complete cancellation of the nonlinear polarizations generated at the two interfaces, thereby yielding a finite effective second-order response in an otherwise centrosymmetric system. The strongly inhomogeneous field distribution may also permit nonlocal bulk-like second-order contributions associated with electric-quadrupole and electric-field-gradient nonlinear polarizations. By contrast, for the WS₂ nanoparticle on the ITO/SiO₂ substrate, as shown in Figure S6c, the absence of coupling to a metallic mirror results in more comparable electric-field intensities at the upper and lower surfaces, with the z -dependent profile exhibiting a substantially smaller contrast between the two interfaces. The resulting weaker top–bottom electromagnetic asymmetry and field inhomogeneity are consistent with the much lower SHG intensity observed from the ITO/SiO₂-supported nanoparticle.

When the excitation wavelength further overlaps with the hybrid nanoparticle–mirror resonance, the SHG response enabled by the mirror-induced asymmetric electromagnetic environment is further enhanced. The second-order nonlinear polarization follows the standard relation [1]: $P_i^{(2)} = \epsilon_0 \sum_{j,k} \chi_{ijk}^{(2)} E_j E_k$, indicating that the nonlinear polarization depends quadratically on the local fundamental field. Correspondingly, when other factors remain

approximately comparable, the SHG intensity scales qualitatively as: $I_{2\omega} \propto |E_{loc}(\omega)|^4$. As shown in Figures S6a and S6b, resonant excitation produces a substantially stronger local fundamental field near the WS₂/SnO₂ interface than that in the Ag off-resonant configuration. Optical resonance can therefore provide an additional SHG enhancement by increasing the electromagnetic energy and local fundamental field within the nonlinear medium. Consequently, among the configurations considered here, the resonant WS₂ nanoparticle on the SnO₂/Ag/SiO₂ substrate exhibits the strongest SHG intensity.

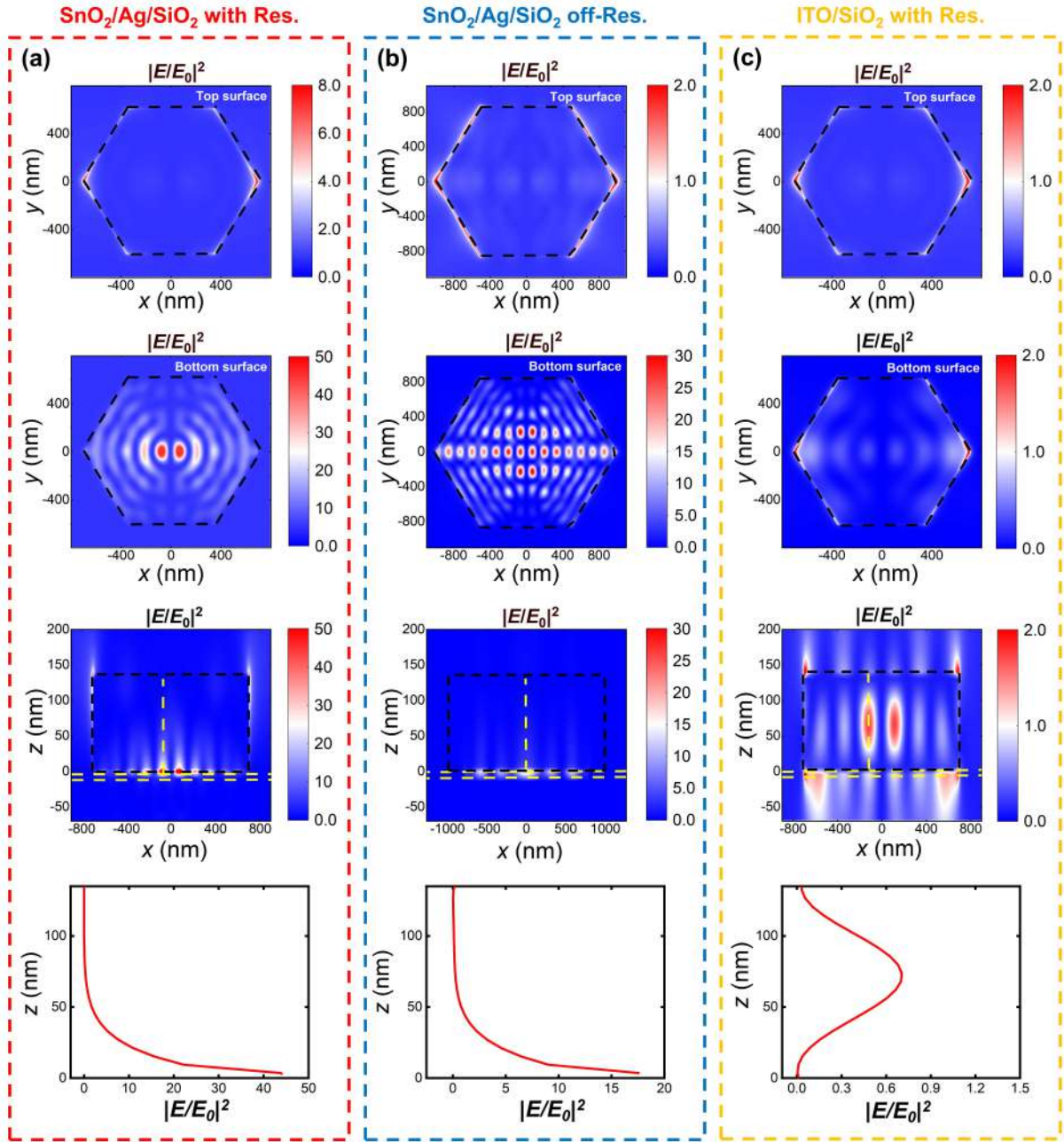


Figure S6. Simulated electric-field intensity distributions, $|E/E_0|^2$, of WS₂ nanoparticles evaluated at 790 nm under different substrate and resonance conditions. (a) For the resonant

WS₂ nanoparticle on the SnO₂/Ag/SiO₂ substrate, the field distributions are shown in the x - y planes at the top ($h = 135$ nm) and bottom ($h = 0$ nm) surfaces, together with the corresponding side-view distribution in the x - z plane. The spatial variation of the electric-field intensity along the vertical yellow dashed line is also plotted. For comparison, (b) presents the field distribution at the same wavelength for a WS₂ nanoparticle on the same SnO₂/Ag/SiO₂ substrate whose resonance wavelength is shifted away from 790 nm, whereas (c) shows the corresponding field distribution for a WS₂ nanoparticle on the ITO/SiO₂ substrate under otherwise identical conditions.

Supplementary Note 7. Optical properties of multilayer WS₂ flake for comparison

Figure S7 shows the optical properties of a multilayer WS₂ (a few tens of nanometers) flake on SnO₂/Ag/SiO₂ substrate for comparison. The optical image of a multilayer WS₂ flake is shown in Figure S7a, where the layer structure can be confirmed. The corresponding scattering spectrum shown in Figure S7b confirms the nature of WS₂, with pronounced excitonic absorption ~ 620 nm. The finite SHG response observed from the multilayer WS₂ flake is consistent with the electromagnetic inequivalence between its upper and lower interfaces in the presence of the SnO₂/Ag/SiO₂ substrate, as shown in Figures S7c and S7d. However, the SHG intensity from the multilayer WS₂ flake is weaker than that from the WS₂ nanoparticles, indicating the electric field enhancement in the WS₂ nanoparticles driven by ED-dominated hybrid nanoparticle–mirror resonance. In addition, the wavelength-dependent SHG spectrum shows the peak at a shorter wavelength (Figure S7d) compared to that of the resonance-driven SHG in WS₂ nanoparticle, as discussed in Figure 4 of the main text.

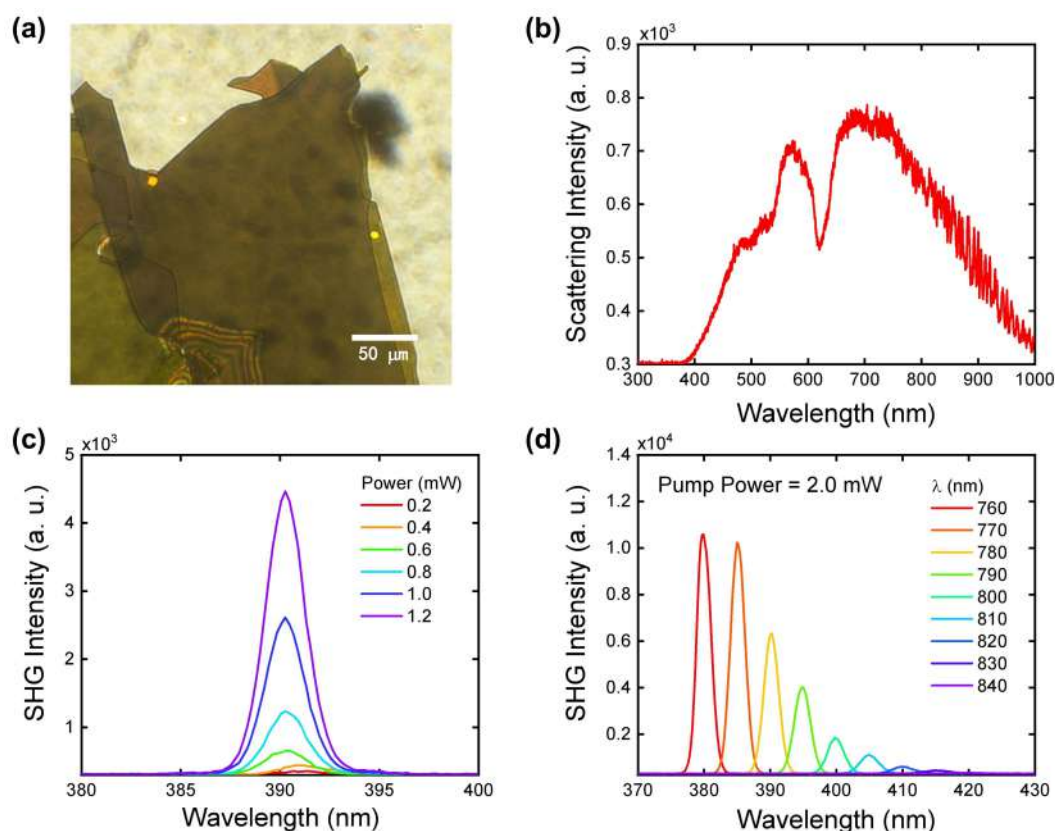


Figure S7. Optical properties of a multilayer flake with a few tens of nanometer thickness. (a) The bright-field image of a multilayer WS₂ flake on SnO₂/Ag/SiO₂ substrate. (b) Scattering spectrum of the WS₂ flake shown on (a). (c) SHG spectra of the multilayer WS₂ flake with varying excitation power at 790 nm. (d) Wavelength-dependent SHG spectra of the multilayer WS₂ flake at an excitation power of 2 mW.

Supplementary Note 8. Original scattering spectra and multipole-decomposition results

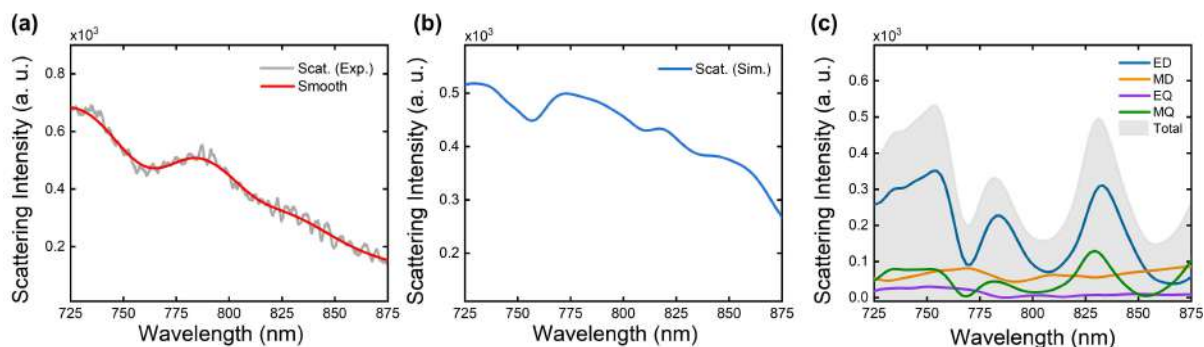


Figure S8. Original scattering spectrum and multipole-decomposition results used for comparison in Figure 3a. (a) Experimentally measured scattering spectrum of a WS₂ nanoparticle on the SnO₂/Ag/SiO₂ substrate. (b) Simulated total scattering spectrum of the same nanoparticle–mirror system. (c) Corresponding multipole-decomposition results. The original datasets shown in (a–c) were individually normalized and then scaled by factors of 0.55, 0.35, and 0.80, respectively, before being overlaid to construct Figure 3a.

Supplementary Note 9. Far-field multipole decomposition and near-field characteristics of the ED-dominated resonance

To further clarify the identification of the resonant mode near 790 nm, we compare the multipole decomposition and the corresponding near-field distributions of WS₂ nanoparticles with two different long-axis lengths. Under the same SnO₂/Ag/SiO₂ substrate environment and with the nanoparticle thickness fixed at $h = 135$ nm, the multipole decomposition of the scattering spectrum for the WS₂ nanoparticle geometry used in the main text ($L = 1200$ nm) is shown in Figure S9a. The ED channel provides the dominant contribution to the far-field scattering near 790 nm, whereas the corresponding electric-field intensity distribution at the WS₂/SnO₂ interface exhibits a more complex spatial pattern than the conventional two-lobed distribution of an isolated electric dipole (Figure S9c). This difference arises because the multipole decomposition characterizes the radiative contributions of the induced current moments, while the near-field distribution reflects the complete spatial electromagnetic response of the finite nanoparticle–mirror system. For the nanoparticle geometry considered here, the finite particle thickness, hexagonal boundary, vertical asymmetry of the substrate environment, and mirror-mediated coupling with the Ag film collectively hybridize the modal field distribution, resulting in a spatial pattern more complex than that of an isolated electric dipole. When the long-axis length of the WS₂ nanoparticle is reduced to $L = 800$ nm, the corresponding resonance blueshifts to 750 nm, as shown by the multipole-decomposed scattering spectrum in Figure S9b, consistent with the size-dependent spectral evolution presented in Supplementary Note 2. Meanwhile, the far-field scattering of this resonance remains dominated by the ED contribution, whereas the electric-field intensity distribution at the WS₂/SnO₂ interface evolves toward a clearer two-lobed pattern (Figure S9d). This size-dependent evolution of the near-field distribution provides further support for assigning the resonance to an ED-dominated mode, while indicating that the more complex spatial field pattern of the nanoparticle used in the main text originates from the geometry- and mirror-mediated modification of its local electromagnetic response. Accordingly, we identify the resonance investigated in this work as an ED-dominated hybrid nanoparticle–mirror resonance rather than a purely ED Mie mode.

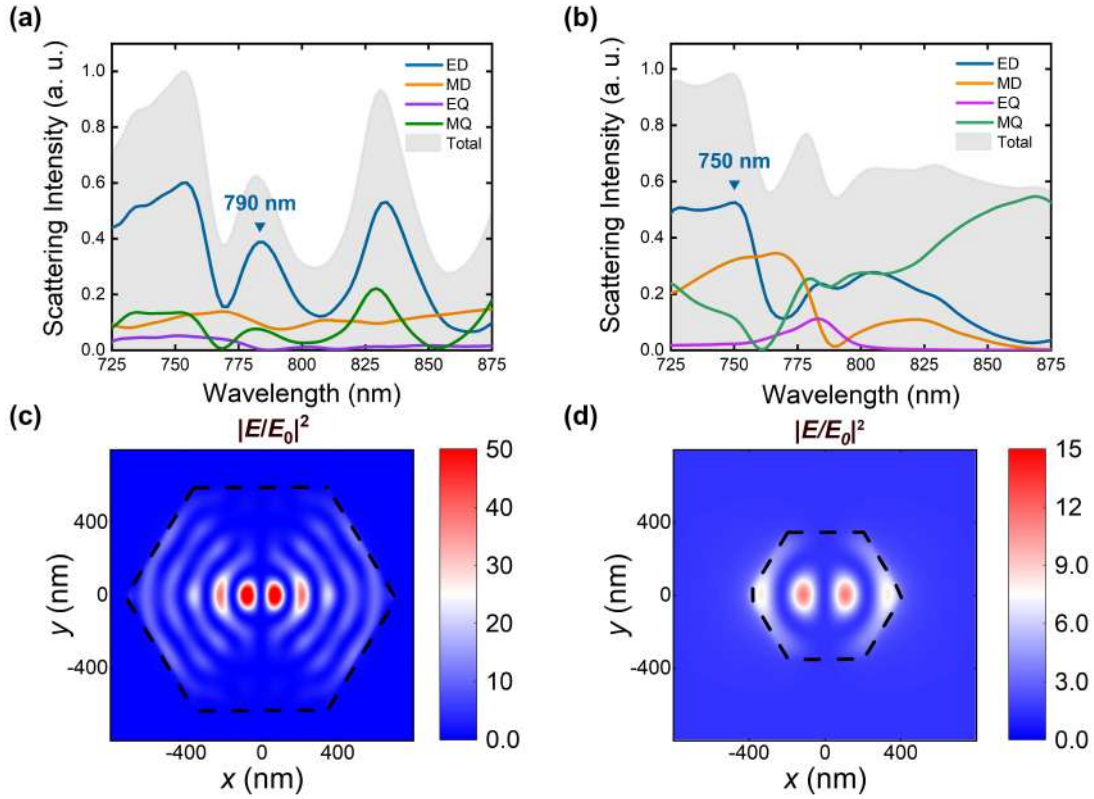


Figure S9. Comparison of the multipole decomposition and near-field distributions of the ED-dominated resonance. (a,c) Multipole decomposition of the scattering spectrum (a) and the corresponding electric-field intensity distribution at the WS₂/SnO₂ interface (c) for the WS₂ nanoparticle geometry used in the main text ($L = 1200$ nm, $h = 135$ nm). (b,d) Corresponding multipole decomposition of the scattering spectrum (b) and electric-field intensity distribution at the WS₂/SnO₂ interface (d) for a WS₂ nanoparticle with a reduced long-axis length of $L = 800$ nm and the same thickness $h = 135$ nm.

Supplementary Note 10. Reproducibility of the power-dependent SHG response

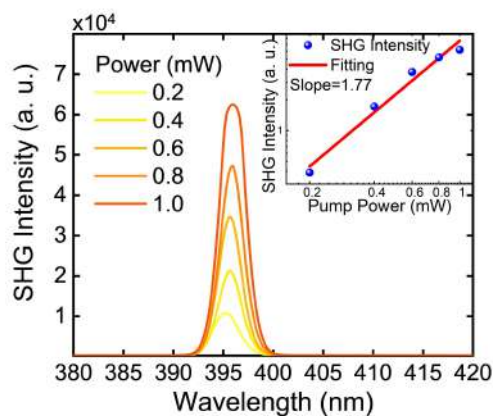


Figure S10. Power-dependent SHG response of an additional WS₂ nanoparticle on the SnO₂/Ag/SiO₂ substrate under 790 nm excitation. The inset shows the SHG peak intensities extracted from the spectra in the main panel as a function of incident power, together with the corresponding power-law fit.

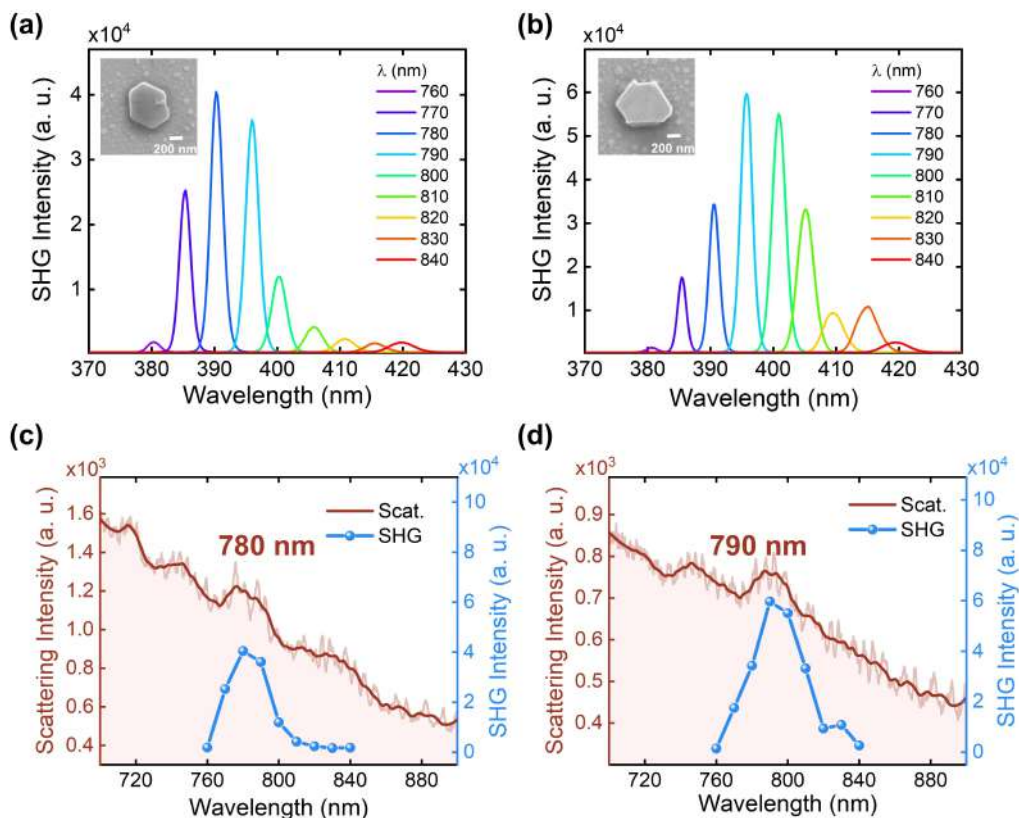
Supplementary Note 11. SHG signals of more examples of WS₂ nanoparticles

Figure S11. SHG responses of two additional WS₂ nanoparticles on the SnO₂/Ag/SiO₂ substrate. (a,b) Excitation-wavelength-dependent SHG spectra of nanoparticles with long-axis lengths L of approximately 794 and 888 nm, respectively. (c,d) Corresponding comparisons between the linear scattering spectra and the excitation-wavelength dependence of the peak SHG intensity for the nanoparticles shown in (a) and (b), respectively. Their resonance wavelengths are approximately 780 and 790 nm, respectively.

References

1. A. Nikitina and K. Frizyuk, "Achiral Nanostructures: Perturbative Harmonic Generation and Dichroism Under Vortex and Vector Beams Illumination," *Advanced Optical Materials* **12**, 2400732 (2024).