

# Revealing Mie Resonances with Enhanced and Suppressed Second-Order Nonlinear Optical Responses in a Hexagonal-Prism-Like MoS<sub>2</sub> Nanoparticle

Mingcheng Panmai, Jin Xiang, Lidan Zhou, Shulei Li, and Sheng Lan\*

Transition metal dichalcogenides (TMDC), such as molybdenum disulfide (MoS<sub>2</sub>), have attracted great interest owing to their excellent electronic and optical properties. Efficient second harmonic generation (SHG) has been successfully demonstrated in the MoS<sub>2</sub> monolayer, in sharp contrast to the negligible SHG from the bulk material. Here, the nonlinear optical responses of hexagonal-prism-like MoS<sub>2</sub> nanoparticles are investigated, which support Mie resonances in the near infrared spectral range. It is revealed that the Mie resonances of such a MoS<sub>2</sub> nanoparticle can be clarified into two types, which exhibit enhanced and suppressed SHG. It is verified that the SHG from the MoS<sub>2</sub> nanoparticle is strongly correlated with the electric field distribution at the optical resonance. For the electric quadrupole mode with an anti-symmetric electric field distribution, the SHG is greatly suppressed. As a result, a nanohole appears in the emission pattern of the SHG from the MoS<sub>2</sub> nanoparticle. In sharp contrast, the SHG from the electric dipole mode with a symmetric electric field distribution can be one order of magnitude stronger than that from a MoS<sub>2</sub> monolayer. The findings open new horizons for manipulating the nonlinear optical responses of TMDC nanoparticles and pave the way for realizing photonic devices.

## 1. Introduction

Using second-order ( $\chi^{(2)}$ ) nonlinear effect to achieve second harmonic generation (SHG) is a popular method for generating coherent light sources at extreme wavelengths. For bulk materials, the phase mismatch between the fundamental wave and the harmonic wave leads to the reduction in the conversion efficiency and various strategies have been proposed to solve this problem. In contrast, phase matching is no longer necessary for nanomaterials whose dimensions are comparable or even smaller than the wavelength of light. In this case, the enhancement of SHG relies mainly on the electric field enhancement at the wavelength of the fundamental wave. Since optical resonances in frequency domain represent the localization of electric field in spatial domain, various optical resonances have been exploited to achieve this goal, including surface plasmon resonances,<sup>[1]</sup> Mie resonances,<sup>[2]</sup>

multipole resonances,<sup>[3,4]</sup> anapole mode,<sup>[5]</sup> Fabry–Perot modes,<sup>[6]</sup> whispering gallery modes,<sup>[7]</sup> epsilon-near-zero resonances,<sup>[8]</sup> and Fano resonances.<sup>[9]</sup> The state-of-the-art researches suggest that surface lattice resonances,<sup>[10]</sup> quasi-bound states in the continuum (quasi-BIC),<sup>[11–15]</sup> and supercavities<sup>[16,17]</sup> can not only realize electromagnetic field enhancement but also suppress radiation loss. The combination of these two features ultimately leads to giant SHG enhancement.

It is well known that SHG is forbidden in a centrosymmetric material with vanishing  $\chi^{(2)}$  nonlinearity. This limitation can be overcome by using nanostructures. At the atomic or molecular level, the discontinuity of atoms on the surface automatically breaks the symmetry of a crystal, leading to an effective  $\chi^{(2)}$  nonlinearity.<sup>[18]</sup> Alternatively, the  $\chi^{(2)}$  nonlinearity can be achieved by using the nonuniformity of the electric field in the nanostructure.<sup>[19]</sup> At the macroscopic level, the  $\chi^{(2)}$  nonlinearity can be obtained by using asymmetric structures.<sup>[20,21]</sup>


So far, the SHG in plasmonic nanoparticles and nanostructures have been extensively studied. Early in 2007, a multipolar tensor analysis for the SHG from a regular array of L-shaped gold nanoparticles was performed. The transmitted and reflected light of the metasurface is analyzed by dividing the tensors into symmetric (dipolar) and anti-symmetric (higher multipolar)

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parts and the nonlinear response is found to be dominated by a tensor component associated with chiral symmetry breaking of the sample.<sup>[22]</sup> In addition, unidirectional nonlinear optical scattering was realized by using an array of V-shaped plasmonic antennas with symmetry breaking.<sup>[21]</sup> By using a plasmonic two-wire transmission line, it was demonstrated that the symmetry of an optical mode alone is sufficient to allow SHG even in a centrosymmetric structure made of a centrosymmetric material.<sup>[23]</sup> Significant enhancement of SHG using the Fano resonances in plasmonic heptamers of silver nanoparticles is theoretically and experimentally demonstrated. The geometry is engineered to simultaneously produce a Fano resonance at the fundamental wavelength and a higher order scattering peak at the second harmonic wavelength.<sup>[24]</sup> Surface second-order nonlinearity of metallic nanoparticles can be significantly boosted up by plasmon-induced field enhancement. However, the far-field SHG may be quenched in highly symmetric plasmonic nanostructures despite huge near-field amplification. It was demonstrated that the SHG from a single gold nanosphere is significantly enhanced when tightly coupled to a metal film. The light-induced electromagnetic asymmetry in the nanogap junction efficiently suppresses the cancellation of locally generated SHG fields. The second harmonic emission is further amplified through preferential coupling to the bright dipolar resonance mode of the nanocavity.<sup>[25]</sup>

In the last decade, the linear and nonlinear optical responses of high-index dielectric nanoparticles (e.g., Si, Ge, GaAs, and AlGaAs nanoparticles) supporting Mie resonances in the visible to near infrared spectral range have received intensive and extensive studies due to their potential applications in photonic devices. The Mie resonances of Si nanoparticles have been exploited to enhance not only the third harmonic generation (THG)<sup>[26]</sup> but also the SHG.<sup>[11]</sup> In addition, it was suggested that the directionality of the SHG emission can be manipulated by engineering the geometry and position of a GaAs nanoantenna.<sup>[27]</sup> Apart from Si nanoparticles, strong SHG was also observed in AlGaAs nanoantennas driven by both electric and magnetic resonances. The contributions of electric and magnetic nonlinear responses can be distinguished by analyzing the structure of polarization states of vector beams in the second harmonic radiation.<sup>[4]</sup> The nonlinear optical response of a dimer composed of two identical dielectric nanoparticles illuminated by a circularly polarized light was also studied. A general theory describing hybridization of multipolar modes of the coupled nanoparticles was developed to reveal nonvanishing nonlinear circular dichroism in the SHG enhanced by the multipolar resonances in the dimer. The multipolar hybridization theory was verified by the experimental results obtained for the AlGaAs dimers placed on an engineered substrate.<sup>[28]</sup>

Recently, the nonlinear optical resonances of Si nanoparticles were re-examined analytically and numerically by considering both the surface and bulk nonlinearities.<sup>[29,30]</sup> It was demonstrated that the multipolar expansion of the radiated field is dominated by dipolar and quadrupolar modes and the interference between them leads to the directivity of the nonlinear scattering.<sup>[29]</sup> After that, the supercavity mode supported by a single subwavelength AlGaAs nanoantenna was proposed to achieve a record-high conversion efficiency, which exceeds two orders of magnitude the value observed at the Mie resonances.<sup>[16]</sup> Highly efficient

SHG from a Si-based metasurface was demonstrated by exploiting the high quality ( $Q$ ) factor of the quasi-BIC supported in the metasurface.<sup>[11]</sup> Very recently, it was demonstrated experimentally that an individual subwavelength dielectric resonator hosting a BIC mode can greatly boost the conversion efficiency of the SHG.<sup>[31]</sup>

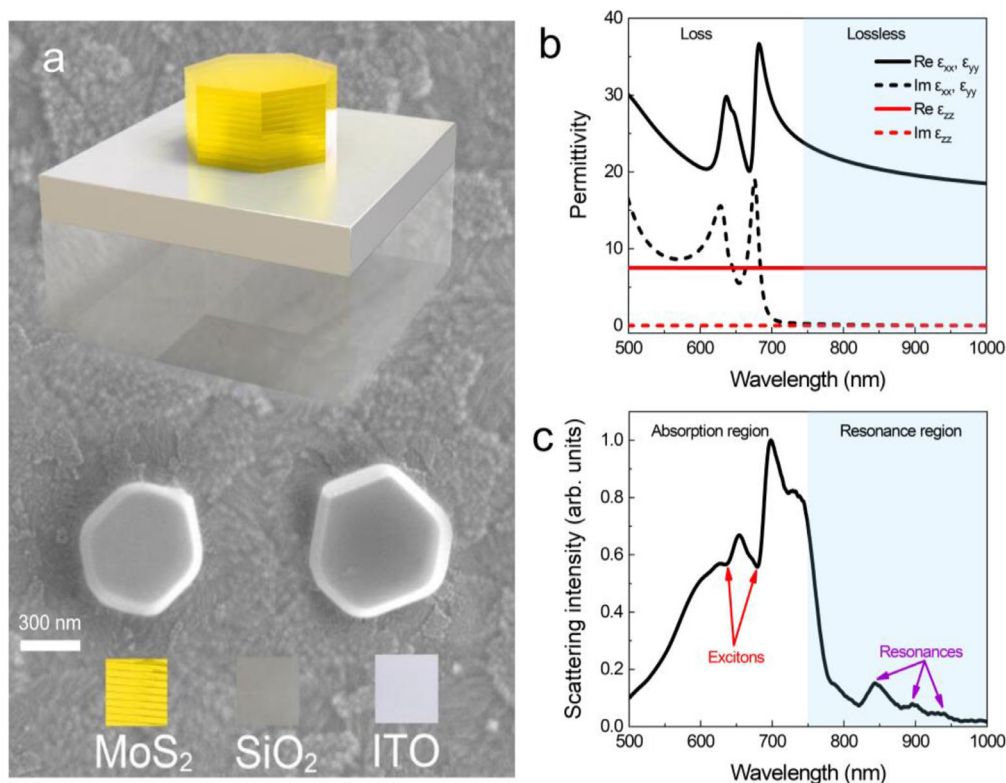
It was recognized recently that transition metal dichalcogenides (TMDCs) possess high refractive indices in the visible and infrared spectral range in addition to their strong nonlinear optical responses. One can achieve highly-confined electromagnetic modes by patterning TMDCs into dielectric resonators.  $WS_2$  disks supporting resonant optical modes were fabricated and they exhibited strong SHG enhancement in the visible light spectrum.<sup>[32]</sup> In addition, the second harmonic emission was spatially directed by using a regular array of  $WS_2$  disks. Moreover, it was found that a metasurface composed of  $MoS_2$  cones exhibits enhanced single-beam SHG and THG.<sup>[33]</sup> It was revealed that the interplay between the resonances of the metasurface allows for tuning of the unidirectional second harmonic wave in forward or backward direction, which is not possible in any bulk nonlinear crystal.

In this article, we investigate the nonlinear optical responses of a hexagonal-prism-like molybdenum disulfide ( $MoS_2$ ) nanoparticle supporting Mie resonances in the near infrared spectral range. We characterize the Mie resonances by measuring the scattering spectrum of the  $MoS_2$  nanoparticle and identify the electric dipole (ED) and electric quadrupole (EQ) modes based on numerical simulations. We examine the SHG at the ED and EQ resonances and correlate the enhanced and suppressed SHG with the electric field distributions in the  $MoS_2$  nanoparticle. We obtain the emission pattern of the second harmonic radiation from the  $MoS_2$  nanoparticle by using laser scanning confocal microscopy and identify clearly the suppressed SHG at the EQ mode. We show that the SHG at the ED mode can be one order of magnitude stronger than that from a  $MoS_2$  monolayer.

## 2. Results and Discussion

In Figure 1a, we show schematically the structure of the  $MoS_2$  nanoparticles studied in this work. They usually appear as hexagonal prisms, which are characterized by an edge length  $l$  and a height  $h$ . For the convenience of morphology characterization,  $MoS_2$  nanoparticles are placed on a silica ( $SiO_2$ ) substrate coated with a thin layer of indium tin oxide (ITO). In the near infrared spectrum, the refractive index of ITO is similar to that of  $SiO_2$  and it has negligible influence on the scattering peaks of a  $MoS_2$  nanoparticle.<sup>[31]</sup> The scanning electron microscopy (SEM) images of two typical  $MoS_2$  nanoparticles are presented in Figure 1a (see the SEM images of more  $MoS_2$  nanoparticles in Note S1, Supporting Information).

In Figure 1b, we present the complex permittivity of  $MoS_2$  used in the numerical simulations reported in this work.<sup>[34]</sup> It is an anisotropic permittivity which considers the difference between the in-plane permittivity and the out-of-plane one. It is noticed that the real part of the in-plane permittivity ( $\text{Re } \epsilon_{xx}, \epsilon_{yy}$ ) is large than 20 in the visible to near infrared spectral range. In comparison, the real part of the out-of-plane permittivity is much smaller.<sup>[35]</sup> For wavelengths longer than 750 nm, the imaginary part of the plane permittivity ( $\text{Im } \epsilon_{xx}, \epsilon_{yy}$ ) approaches zero. It



**Figure 1.** Structure and optical characterization of MoS<sub>2</sub> nanoparticles. a) Schematic showing the structure of a hexagonal-prism-like MoS<sub>2</sub> nanoparticle placed on an ITO/SiO<sub>2</sub> substrate. Also shown are the SEM images of two MoS<sub>2</sub> nanoparticles. b) Complex permittivity of bulk MoS<sub>2</sub> taken from literature. c) Scattering spectrum measured for a typical MoS<sub>2</sub> nanoparticle.

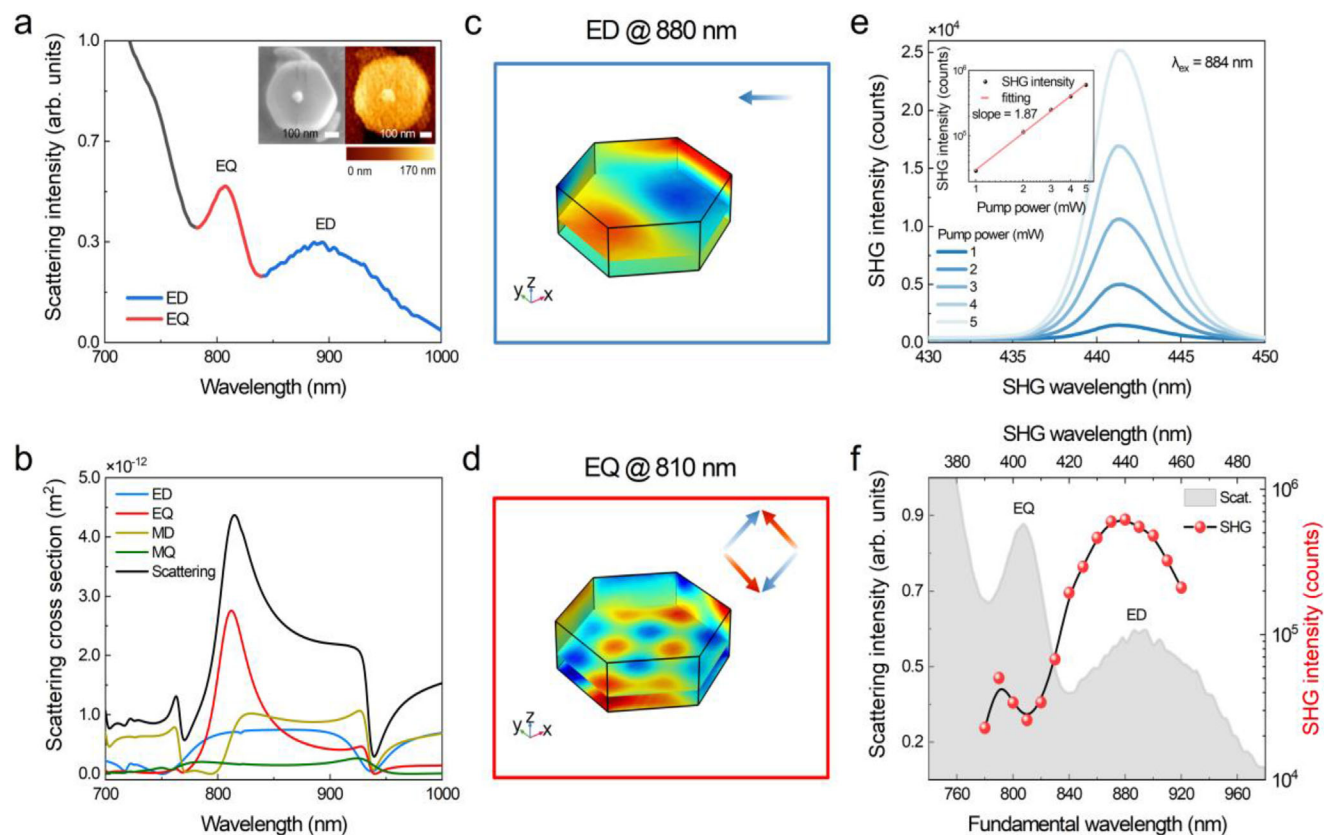
implies MoS<sub>2</sub> becomes a lossless dielectric material with a high refractive index. As a result, MoS<sub>2</sub> nanoparticles may support optical resonances with high *Q* factors in near infrared spectral range.<sup>[36–38]</sup>

In Figure 1c, we show the scattering spectrum measured for typical a MoS<sub>2</sub> nanoparticle in the wavelength range of 500–1000 nm. It can be divided into two regions, i.e., an absorption region and a resonance region. In the absorption region, one can identify clearly two exciton resonances, which appear as two scattering dips in the scattering spectrum. They correspond to the A- (≈615 nm) and B-exciton (≈663 nm) in MoS<sub>2</sub> (see more scattering spectra in Note S2, Supporting Information). It is noticed that a strong scattering peak appears at ≈700 nm in the scattering spectrum. It is caused by the largest real part of the permittivity of MoS<sub>2</sub> at this wavelength and the rapid decrease of the imaginary part after this wavelength. It is noticed that the intensities of the scattering peaks in the resonance region are weaker than those in the absorption region. The dramatic reduction of the real part of the permittivity is responsible for this behavior. In this work, we focus mainly on the low-order Mie resonances appearing as scattering peaks in the resonance region. Since the real part of the permittivity decreases rapidly from We will inspect the SHG efficiencies at these optical resonances so that the SHG is not affected by the exciton resonances.<sup>[39–41]</sup> The high-order Mie resonances of the MoS<sub>2</sub> nanoparticle, which appear in the absorption region, are expected to have low *Q* factors.<sup>[42]</sup> This strategy allows

us to analyze independently the effects of the optical resonances on the SHG of the MoS<sub>2</sub> nanoparticle.

In Figure 2a, we show the scattering spectrum measured for a MoS<sub>2</sub> nanoparticle in the resonance region. The SEM and atomic force microscopy (AFM) images, which are used to characterize the morphology of the MoS<sub>2</sub> nanoparticle, are provided in the insets. The edge length and the height of hexagonal prism are found to be *l* ≈ 300 nm and *h* ≈ 170 nm, respectively. One can identify two optical resonances in the scattering spectrum, which originate from the radiations of the ED mode (≈880 nm) and the EQ mode (≈810 nm) supported by the MoS<sub>2</sub> nanoparticle.

We simulated the scattering spectrum of the MoS<sub>2</sub> nanoparticle based on its structural parameters (*l* = 300 nm, *h* = 170 nm), as show in Figure 2b (see more simulation results Note S3 and S4, Supporting Information). The two optical resonances (ED and EQ modes) can be observed in the scattering spectrum. However, their wavelengths are redshifted by ≈10 nm with respect to the measured ones. In addition, the *Q* factors of the two modes are different in the measured and simulated scattering spectra. There are two reasons accounting for these discrepancies. One is the permittivity of MoS<sub>2</sub> and the other is the imperfection of the MoS<sub>2</sub> nanoparticle. In this work, the complex permittivity of bulk MoS<sub>2</sub> reported in literature is used in the numerical simulation. The actual permittivity of MoS<sub>2</sub> nanoparticle may be different from the reported value. In addition, it is noticed from the SEM and AFM images that the morphology of the



**Figure 2.** SHG efficiencies at different optical resonances. a) Scattering spectrum measured for a MoS<sub>2</sub> nanoparticle in the resonance region. The SEM and AFM images of the MoS<sub>2</sub> nanoparticle are shown as insets. b) Scattering spectrum simulated for a MoS<sub>2</sub> nanoparticle with  $l = 300$  nm and  $h = 170$  nm. c) Electric field distribution calculated for the ED mode of the MoS<sub>2</sub> nanoparticle shown in b) located at 880 nm. The arrow indicates the dipole moment. d) Electric field distribution calculated for the EQ mode the MoS<sub>2</sub> nanoparticle shown in b) located at 810 nm. The arrows indicate the dipole moments. e) SHG intensities measured for the MoS<sub>2</sub> nanoparticle shown in a) in the wavelength range of 780–920 nm. The scattering spectrum of the MoS<sub>2</sub> nanoparticle is provided for reference. f) SHG spectra measured for the MoS<sub>2</sub> nanoparticle shown in a) at an excitation wavelength of  $\lambda_{\text{ex}} = 880$  nm with different pumping powers. The dependence of the SHG intensity on the pump power is presented in the inset.

MoS<sub>2</sub> nanoparticle deviates from a perfect hexagonal prism. In Figure 2c,d, we present the electric field distributions calculated for the ED and EQ modes located at  $\approx 880$  nm and  $\approx 810$  nm, indicating clearly the dipole moment in the ED mode and the four anti-parallel dipole moments in the EQ mode.

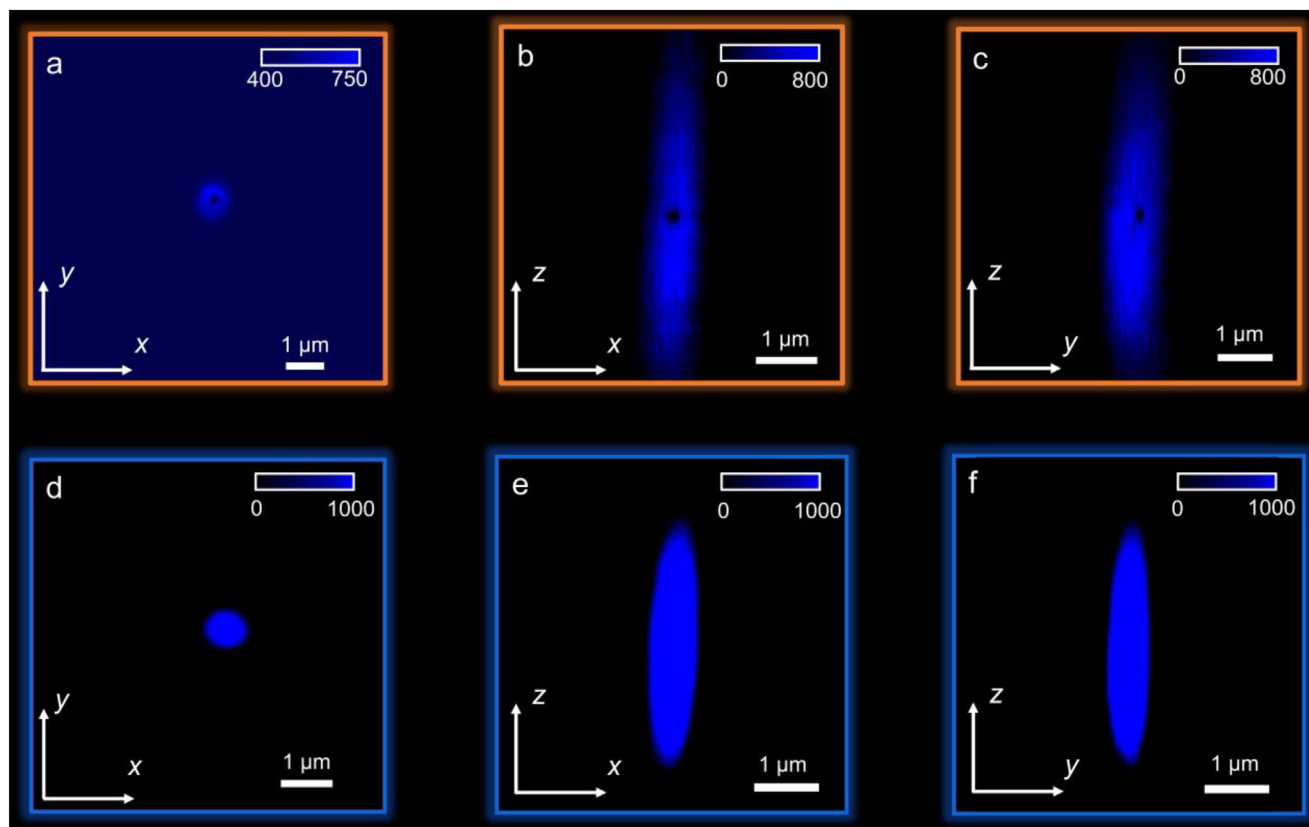
In Figure 2e, we show the SHG spectra obtained by resonantly exciting the ED mode with femtosecond laser pulses of different powers. The dependence of the SHG intensity on the pumping power, which is plotted in a logarithmic coordinate, is presented in the inset. A linear relationship with a slope of  $\approx 1.87$  is observed, indicating clearly the quadratic dependence of the SHG intensity on the intensity of the fundamental wave. We fixed the pumping power at  $P = 5.0$  mW and examined the SHG intensities at different excitation wavelengths, as shown in Figure 2f (see Note S5, Supporting Information).

One can observe a maximum value at  $\approx 880$  nm and a minimum value at  $\approx 810$  nm, which corresponding exactly to the ED and EQ resonances in the scattering spectrum. Interestingly, the SHG intensity at the ED resonance is larger than that at the EQ resonance by a factor of  $\approx 30$ . It means that the SHG of the MoS<sub>2</sub> nanoparticle is enhanced at the ED resonance but suppressed at

the EQ resonance, although the electric field is enhanced in both cases.

For a centrosymmetric material, the gradient of electric field can be generated by an optical mode which breaks the dipole approximation at the atomic level, providing an effective bulk  $\chi^{(2)}$  nonlinearity.<sup>[19]</sup> In general, a larger electric field gradient is anticipated for a high-order optical mode. Basically, one can use the fourth power of the integration of the electric field over the volume of a nanoparticle (i.e.,  $\int |E|^4 dV$ ) to characterize the SHG intensity of the nanoparticle.<sup>[20]</sup> In this regard, a high-order mode is also expected to have a larger integration of the electric field when comparing with a low-order one. However, we are surprised to find that the SHG intensity of the MoS<sub>2</sub> nanoparticle at the EQ resonance is much smaller than that at the ED resonance. As shown in Figure 2d, the EQ mode is composed of two paired dipole moments with equal amplitudes and opposite phases (or anti-parallel dipole moments), leading to the cancellation of the SHG in the far field due to the destructive interference of the radiations from the anti-parallel dipole moments.

The above results can be explained by comparing with the nonlinear optical responses of monolayer and multilayer MoS<sub>2</sub>.



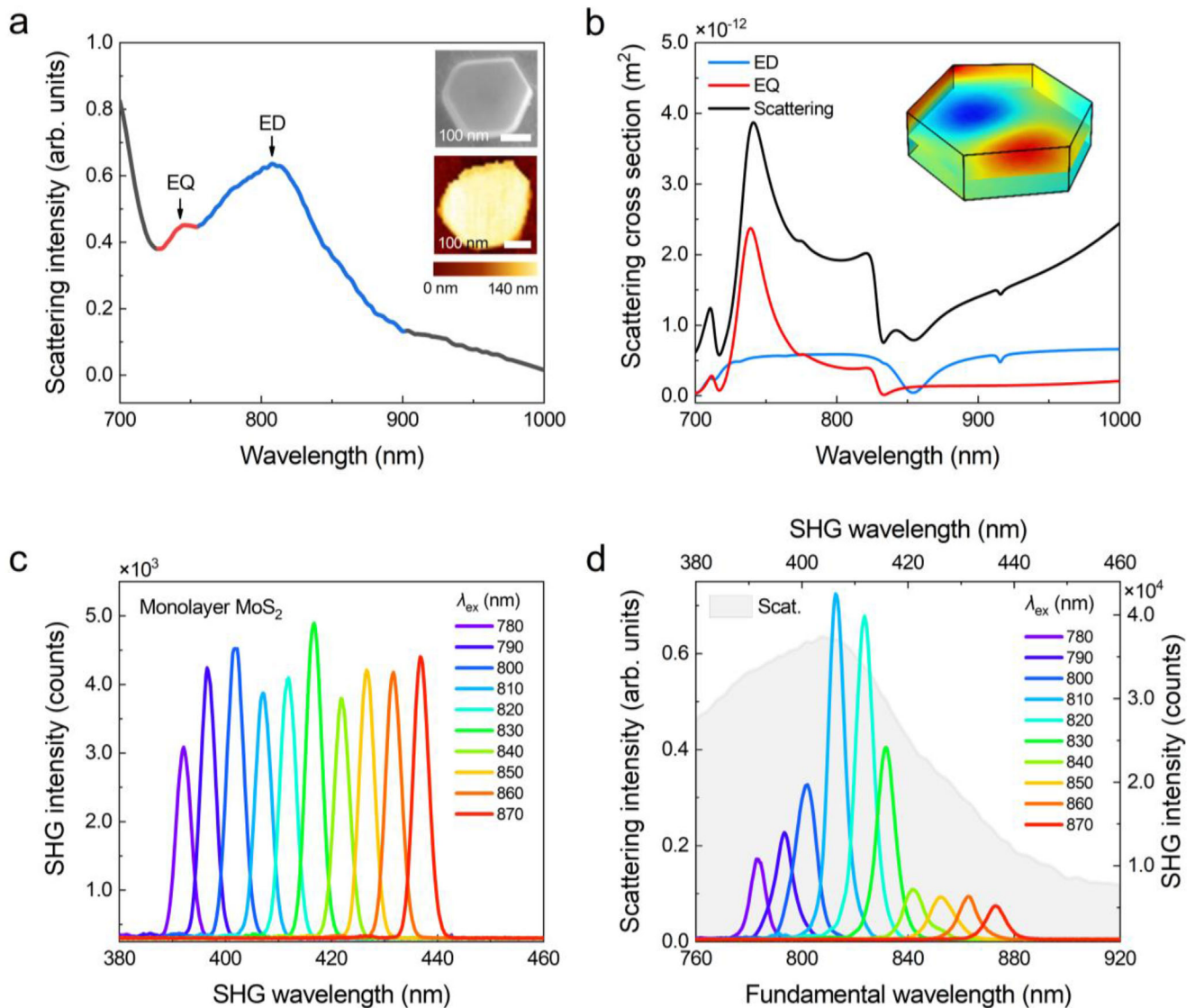
**Figure 3.** Emission patterns of the second harmonic wave observed at different optical resonances. a–c) 2D distributions of SHG intensity on the  $x$ – $y$ ,  $x$ – $z$ , and  $y$ – $z$  planes obtained for a  $\text{MoS}_2$  nanoparticle at the EQ resonance. d–f) 2D distributions of SHG intensity on the  $x$ – $y$ ,  $x$ – $z$ , and  $y$ – $z$  planes obtained for a  $\text{MoS}_2$  nanoparticle at the ED resonance. In both cases, the excitation wavelength was fixed at 800 nm.

Basically, a  $\text{MoS}_2$  monolayer can be regarded as a horizontal dipole, providing an atomic-level  $\chi^{(2)}$  nonlinearity source.<sup>[43]</sup> In comparison, there exist two  $\chi^{(2)}$  nonlinearity sources with the same dipole moment but completely opposite phase in a bilayer  $\text{MoS}_2$ .<sup>[44]</sup> The interference of the radiations from these two anti-parallel dipole moments leads to the cancellation of the SHG signal in the far field.<sup>[45]</sup> For this reason, SHG is generally forbidden in a  $\text{MoS}_2$  wafer with even layers but is allowed in that with odd layers.<sup>[46,47]</sup> This interpretation can be readily extended to the optical modes supported by a  $\text{MoS}_2$  nanoparticle, as studied in this work. The SHG will be enhanced for optical modes with symmetric electric field distributions and suppressed for those with anti-symmetric electric field distributions. We have examined the nonlinear optical responses at the optical resonances of a few  $\text{MoS}_2$  nanoparticles and verified the above conclusion by experimental observations (see Note S6 and S7, Supporting Information).

As discussed above, the surface and bulk nonlinearities of a  $\text{MoS}_2$  nanoparticle contribute simultaneously to the SHG of the  $\text{MoS}_2$  nanoparticle.<sup>[32,48]</sup> For an optical mode with an anti-symmetric electric field distribution, such as the EQ mode, the bulk nonlinearity is expected to vanish and only the surface nonlinearity is left. As a result, a suppressed SHG is anticipated at the EQ resonance.

Recently, optical far-field imaging has emerged as a powerful tool to characterize light-matter interaction and it has been

successfully employed to observe self-coherent multipoles<sup>[49]</sup> and SHG.<sup>[25]</sup> In this work, we examined the SHG of a  $\text{MoS}_2$  nanoparticle by using a confocal laser scanning microscope. In this way, the second harmonic wave emitted from the  $\text{MoS}_2$  nanoparticle was spatially revealed by scanning the laser light across the  $\text{MoS}_2$  nanoparticle, which is equivalent to position the  $\text{MoS}_2$  nanoparticle at different positions of the laser beam with a Gaussian intensity distribution. The excitation wavelength was chosen at the EQ resonance of the  $\text{MoS}_2$  nanoparticle. We examined the 3D SHG intensity of a  $\text{MoS}_2$  nanoparticle resonantly excited at the EQ resonance ( $\approx 800$  nm) (see Note S8, Supporting Information). The origin of the coordinate was chosen at the center of the  $\text{MoS}_2$  nanoparticle. The 2D SHG intensity distributions in the  $x$ – $y$ ,  $y$ – $z$ , and  $x$ – $z$  planes are presented in **Figure 3a–c**, respectively. It is worth noticing that a nanohole corresponding to the disappearance of the SHG was observed when of the  $\text{MoS}_2$  nanoparticle is located at the center of the laser beam. In addition, the size of the nanohole is comparable to that of the nanoparticle. This behavior indicates that the SHG in this case arises mainly from the surface nonlinearity and the contribution from the bulk nonlinearity is negligible. (see more scanning results in Note S9, Supporting Information). For comparison, we also inspected the 3D distribution of the SHG intensity at the ED resonance of another  $\text{MoS}_2$  nanoparticle located at  $\approx 800$  nm (i.e., the wavelength of the femtosecond laser light) (see Note S8, Supporting Information). The corresponding 2D distributions in the  $x$ – $y$ ,  $y$ – $z$ , and  $x$ – $z$  planes are



**Figure 4.** Enhanced SHG at the ED resonance. a) Scattering spectrum measured for a MoS<sub>2</sub> nanoparticle. The SEM and AFM images are shown as insets. b) Scattering spectrum simulated for the MoS<sub>2</sub> nanoparticle shown in (a). The electric field distribution is shown in the inset. c) SHG spectra measured for a monolayer MoS<sub>2</sub> at different pumping wavelengths ranging 780–870 nm. d) SHG spectra measured for a MoS<sub>2</sub> nanoparticle at different pumping wavelengths around the ED resonance. The scattering spectrum of the MoS<sub>2</sub> nanoparticle is provided for reference. In all cases, the pumping power was fixed at  $P = 5.0$  mW.

shown in Figure 3d–f. Apart from the increase in the SHG intensity, the nanohole observed previously disappeared completely.

For the ED resonance, both the surface and the bulk nonlinearity will contribute to the SHG. In this case, the SHG can be regarded as the radiation of a single dipole moment with greatly enhanced intensity. In Figure 4a, we show the scattering spectrum measured for a hexagonal-prism-like MoS<sub>2</sub> nanoparticle. The ED resonance of the MoS<sub>2</sub> nanoparticle appears at ≈810 nm. The SEM and AFM images of the nanoparticle are shown as insets. It can be seen that the shape of the MoS<sub>2</sub> nanoparticle deviates from a perfect hexagonal prism. Based on the structural parameters extracted from the morphology characterization, we calculated the scattering spectrum of the MoS<sub>2</sub> nanoparticle, as shown in Figure 4b. The simulated scattering spectrum is in qualita-

tively agreement with the measured one. The discrepancy originates mainly from the accuracy of the complex permittivity used in the numerical simulation. Based on the multipole decomposition of the scattering spectrum, it is revealed that the small scattering peak appearing on the left shoulder of the ED resonance (≈750 nm) originates from the EQ mode. In order to verify the enhancement in the SHG achieved at the ED resonance, we first examined the SHG spectra for a MoS<sub>2</sub> monolayer at different excitation wavelengths, as shown in Figure 4c. In this case, a MoS<sub>2</sub> monolayer was transferred onto the same ITO/SiO<sub>2</sub> substrate used to support the MoS<sub>2</sub> nanoparticle (see Note S10, Supporting Information). It was found that the SHG intensity is not sensitive to the excitation wavelength which was changed from 780 to 870 nm. In Figure 4d, we present the SHG spectra measured for

the MoS<sub>2</sub> nanoparticle at different excitation wavelengths around the ED resonance. As expected, it was found that the SHG intensity depends strongly on the excitation wavelength and the maximum SHG was observed at the ED resonance ( $\approx 810$  nm). More importantly, it was found that the SHG intensity measured for the MoS<sub>2</sub> nanoparticle at the ED resonance was  $\approx 8.0$  times stronger than that observed for the MoS<sub>2</sub> monolayer, which confirms undoubtedly the enhanced SHG at the ED resonance.

In order to examine the effects of Mie resonances on the SHG efficiency in MoS<sub>2</sub> nanoparticle with regular shapes, we also fabricated MoS<sub>2</sub> nanodisks from a MoS<sub>2</sub> film grown by chemical vapor deposition with the combination of electron beam lithography and reactive ion etching (see Note S11, Supporting Information). Unfortunately, no SHG was detected when such MoS<sub>2</sub> nanodisks were excited by using femtosecond laser pulses. We compared the X-ray diffraction spectra of the hexagonal-prism-like MoS<sub>2</sub> nanoparticles and the MoS<sub>2</sub> nanodisks. It was found that the hexagonal-prism-like MoS<sub>2</sub> nanoparticles are crystalline while the MoS<sub>2</sub> nanodisks are polycrystalline (see Note S11, Supporting Information). This is the reason why no SHG was observed for the MoS<sub>2</sub> nanodisks.

### 3. Conclusion

In conclusion, we have investigated the SHG of hexagonal-prism-like MoS<sub>2</sub> nanoparticles supporting Mie resonances in the near infrared spectral range. It was found that the SHG is enhanced at the ED resonance and suppressed at the EQ resonance. The enhanced and suppressed SHG originate from the symmetric and anti-symmetric electric field distributions in the ED and EQ modes. The disappearance of the bulk nonlinearity was clearly revealed in the radiation pattern of the SHG obtained by using a confocal laser scanning microscope. Moreover, it was found that the SHG intensity at the ED resonance is enhanced by a factor of  $\sim 8.0$  as compared with that of MoS<sub>2</sub> monolayer. Our findings indicate the importance of the mode profile in determining the nonlinear optical responses of high-index nanoparticles and suggest the potential applications of such nanoparticles in nonlinear optical devices.

### 4. Experimental Section

**Sample Fabrication:** The MoS<sub>2</sub> nanoparticles and MoS<sub>2</sub> monolayers used in this work were purchased from Sixcarbon Tech Shenzhen. They were synthesized by using chemical vapor deposition. Hexagonal-prism-like MoS<sub>2</sub> nanoparticles were obtained by dispersing MoS<sub>2</sub> nano-powders uniformly in water and centrifuging the aqueous solution.

**Optical Measurements:** The linear and nonlinear optical responses of MoS<sub>2</sub> nanoparticles were characterized by using an inverted microscope (Observer A1, Zeiss) equipped with white light and femtosecond laser light as excitation sources.

A dark-field microscope with a home-built oblique incidence system was employed to characterize the scattering properties of MoS<sub>2</sub> nanoparticles. In this case, the illumination light was incident on MoS<sub>2</sub> nanoparticles at an angle of  $\approx 40^\circ$  and the forward scattering light was collected by the objective of the dark-field microscope.

The MoS<sub>2</sub> nanoparticles were excited by the femtosecond laser light focused with the 100 $\times$  or 60 $\times$  objective of the microscope. The SHG signals were gathered by the objective and directed to a spectrometer (SR-500i-B1, Andor) for spectral analysis or to a charge-coupled device (DU970N, An-

dor) for imaging. The mapping of the SHG signals from MoS<sub>2</sub> nanoparticles was performed by using a confocal laser scanning microscope (A1MP, Nikon).

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Keywords

laser scanning confocal microscopy, Mie resonance, nanoparticles, second harmonic generation, transition metal dichalcogenides

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