Localization-enhanced second harmonic generation in twisted WS$_2$ spirals

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Abstract

In moiré crystals formed by stacking twisted two-dimensional (2D) layered materials, surprisingly diverse correlated optical and electrical properties can be realized by a subtle change in twisted angle. In this work, we report the observation of localization-enhanced second harmonic generation (SHG) in twisted WS$_2$ spirals, thereby adding insight into moiré physics. The twisted WS$_2$ spirals with various twisted angles are synthesized on a Euclidean or non-Euclidean surface by a well-designed water-assisted chemical vapor deposition. Compared to WS$_2$ monolayer, the minimum and maximum SHG signals in different regions of the twisted WS$_2$ spirals are enhanced by a factor of 4–12 and 26–136 at similar thickness, respectively, as the twisted angle between adjacent layers decreases from 20° to ≈ 0°. The significant SHG enhancement is explained by the evolution of structural symmetry and moiré potentials in these WS$_2$ spirals at different twisted angles. Their layer-dependent photoluminescence and Raman spectra show significantly changed peak position and intensity, confirming the strong local confinement effect of moiré potentials in these spirals. These findings provide an efficient method for the rational growth of 2D moiré structures and the implementation of a localization-enhanced SHG, endowing them great potential for exploring strong coupling correlation physics and applications in twistronics.

Introduction

The emerging twisted van der Waals (vdW) structures offer a variety of attractive building blocks for the study of various extraordinary physical phenomena$^1$–$^5$. For example, the twisted vdW structures with multiple vertically stacked layers create periodic moiré lattices due to lattice mismatches or twisted angles$^6$. The moiré potential of these moiré lattices determines the dynamics within the mini-Brillouin zone$^7$–$^9$, which induces strongly correlated quantum phenomena ranging from moiré excitons$^{10}$–$^{13}$, moiré phonons$^{14,15}$ and an enhanced photoresponse$^{16,17}$ in optics to superconductivity,$^1$ as well as ferromagnetism$^{18}$ and fractional quantum Hall effects$^{19,20}$ in electronics. In particular, the moiré lattices in twisted vdW structures feature an almost arbitrary geometry that is consistent with the crystallographic symmetry groups of the sublattices, and therefore offer a new avenue for quantum manipulation of quasiparticles in quantum optics. Recently, the supertwisted spiral moiré lattices in twisted WS$_2$/WSe$_2$ spirals were resolved, enabling special angle-dependent moiré patterns$^{21}$. These angle-dependent twisted vdW structures hold promise for exploring the strong coupling correlation physics of twistronics$^{22,23}$, including optics, electronics, acoustics, condensed matter and quantum physics$^{24}$. However, the relationship between the second harmonic generation (SHG) effect of 2D twisted vdW structures and the twisted angle of the layers needs further investigation, particularly for 2D twisted spirals with more than two layers.

Here we investigate the evolution of the SHG effect in twisted WS$_2$ spirals based on the angular degree of freedom. We present the experimental realization of twisted spiral moiré lattices with controllable twist angles and symmetry. The twisted spiral WS$_2$ lattices are obtained by screw-dislocation-driven (SDD) growth with hexagonal primitive cells and have a tunable twisted angle. Depending on the twisted angle,
spiral moiré lattices with a different periodic structure enable a localized moiré potential at the interface and thus a localization-enhanced SHG effect. Furthermore, the layer-dependent SHG spectra show that the distinguishable intensity is a result of the evolution of structural symmetry. By combining the variation of the SHG effect with the characterization of photoluminescence (PL) and Raman spectra, the formation of the confinement effect of moiré potentials is created by the moiré lattices. Overall, these findings pave a new path to manipulate the localization of the moiré potential in 2D twisted spiral structures for further studies in strongly correlated physics and twistronics.

Results and Discussion

One-step growth of twisted WS$_2$ Spirals

In typical chemical vapor deposition (CVD)$^{25,26}$, the WS$_2$ spirals are grown on a flat SiO$_2$/Si substrate. During the growth, the lattice would follow the geometry of the substrate, therefore the WS$_2$ spiral grows into a stacked triangle with the edges of different layers aligned in parallel (Fig. S1a-c)$^{27,28}$. However, when the screw dislocation locates on a protrusion which is a non-Euclidean surface, the screw dislocation driven growth would result in a very different morphology called supertwisted spirals (Fig. S1d-k)$^{21}$. The growth of supertwisted WS$_2$ spirals is enabled by the geometric mismatch between the Euclidean crystal lattice and a curved non-Euclidean surface, which causes the adjacent layers to have roughly the same twist angle relative to each other (Fig. S2)$^{21}$.

The growth of twisted WS$_2$ spirals was achieved by a water vapor-assisted CVD process (Fig. S3). Briefly, WS$_2$ powder was filled in a quartz boat and then placed in the heating center of the furnace, and a silicon substrate with 280 nm SiO$_2$ was placed downstream for material deposition (See Materials and Methods for growth details). The key step in the growth of twisted spiral WS$_2$ is the introduction of deionized water. In particular, 0.05–0.1 ml deionized water was dropped onto the edge of another quartz boat. This keeps the water droplets in an elliptical shape and prevents them from evaporation before heating. The boat with water was then placed 20–25 cm upstream from the WS$_2$ powder (outside the insulation of the tube furnace to prevent the deionized water from evaporating too quickly when heated). In previous work, we have demonstrated that the water here can serve as a transport agent to promote the dissociation and volatilization of the WS$_2$ precursor$^{26}$ by forming volatile WO$_x$(OH)$_y$ gas species and H$_2$S gas. Those gas species lead to increased vapor pressure and, accordingly, increased nucleation. The volatile WO$_x$(OH)$_y$ can also decompose and from WO$_x$ particles, which tends to form on the edge of the growing WS$_2$, which act as a conical surface and form a non-Euclidean substrate. As growth proceeds, the continuously supplied vapor species from the precursor enable additional nucleation and growth on the newly formed ribbons, ultimately forming the supertwisted WS$_2$ spirals (Fig. S4a-f). This growth method is cost-effective and efficient enough to grow high-quality twisted WS$_2$ spirals.
Figure 1a shows a typical optical image of the twisted WS\textsubscript{2} spiral with a small twisted angle $\approx$ 0° grown on a Euclidean surface (screw dislocation is far away from the non-Euclidean surface). A well-defined triangular shape and a spiral arm at the edge are resolved. The corresponding atomic force microscopy (AFM) image (Fig. 1b) further shows that the twisted WS\textsubscript{2} spiral has undergone a rotating upward growth behavior and the edges of different layers are nearly aligned in parallel. Figure 1c and 1d are the optical and AFM images of the right-handed supertwisted WS\textsubscript{2} spirals (screw dislocation is located at non-Euclidean surface), respectively. The height of the colored band on top of the WS\textsubscript{2} spiral is about 0.7 nm (Fig. 2d). This number corresponds to the thickness of a WS\textsubscript{2} monolayer, proving the existence of a WS\textsubscript{2} ribbon underneath the WS\textsubscript{2} spiral. Fig. S5 provides more details of the left/right-handed supertwisted WS\textsubscript{2} spirals. Moreover, we found that the twisted angle of the supertwisted WS\textsubscript{2} spiral can be adjusted by the angle $\alpha$ of the shear sector. Figure 1g shows typical growth models with a twisted angle $\alpha$ of $\pm$ 10°, $\pm$ 15° and $\pm$ 20°. Under an optical microscope, the twisted spirals with near zero angles have triangular shapes (Fig. 1a, 1b), while the spirals with large twisted angles show a circular or spiral shapes (Fig. 1c-f and Fig. S6a-d). The circular shape, which results from the envelope curves of the three sets of edges, is consists of three Archimedean spiral curves\textsuperscript{21}. This is a good indication of the twisted superstructures. Therefore, the optical microscope allows us to quickly identify the spirals with different twisted angles.

**Twist angle-dependent nonlinear optical effects**

Next, the nonlinear optical properties of these WS\textsubscript{2} spirals were examined. In principle, the relationship between the angle-dependent SHG of WS\textsubscript{2} spirals and the number of layers can be investigated using the reflection mode of an optical microscope (Fig. 2 and Fig. S7). However, since the lateral size of the supertwisted WS\textsubscript{2} spirals (~ 10 µm) is close to the size of the laser spot (~ 2 µm), it is difficult to accurately identify the SHG signals from specific layers. Alternatively, here we use the layer thickness identified in the optical images (marked with colorful crosses, R1-R5, in Fig. 2) to qualitatively distinguish the number of WS\textsubscript{2} layers. The layer-dependent SHG intensity of twisted WS\textsubscript{2} spirals shows that all regions have a remarkable SHG signal (Fig. 2).

For example, Fig. 2a-c show that the SHG intensity increases with increasing number of layers, and the maximum SHG signal in Region 5 is enhanced over 136 times compared to WS\textsubscript{2} monolayer (Table 1 and Fig. S8). Figure 2d-l show the oscillating SHG intensity with increasing number of layers and twisted angles. Even though, the SHG intensity of the supertwisted spirals is always higher than that of monolayer WS\textsubscript{2} (Table 1). For example, in the supertwisted WS\textsubscript{2} spiral with a twisted angle of 13° (Fig. 2d-f), the SHG intensity in Region 1–3 (R1, R2, R3) gradually increases from 5 times to 40 times as layer number increases compared to monolayer WS\textsubscript{2}, just like the WS\textsubscript{2} spiral with 3R phase. However, the SHG intensity decreased rapidly in Region 4–5 (R4, R5). The SHG intensity of the supertwisted WS\textsubscript{2} spiral with a twisted angle of 16° (Fig. 2g-i) and 20° (Fig. 2j-l) shows the same decreasing law. The small increase in Region 4 (Fig. 2l) results from the interference of external noise with the error margin. Another interesting observation is that the onset of SHG decline region changes from Region 3 to Region 2 to Region 1 as the twisted angle increases from 13° to 16° to 20°, respectively. Overall, depending on the
twisted angles and layers, the SHG signal can be amplified 12–136 times for ≈ 0° spirals\textsuperscript{29,30}, 4–92 times for 13° spirals, 10–42 times for 16° spirals, and 4–26 times for 20° spirals, respectively (Table 1). Both the maximum and minimum enhancement factors decrease with increasing twisted angles. These results are caused by the evolution of inversion symmetry, moiré potential and strain at varying twisted angles, which are explained as follows.

The twisted WS\textsubscript{2} spiral in Fig. 2a is a twisted 3R phase structure with strain induced during SDD growth\textsuperscript{31}, resulting in a near zero twisted angle (≈ 0°) between two adjacent layers. The twisted 3R structure is an inversion symmetry broken structure\textsuperscript{27}. Meanwhile, as a result of this small twisted angle, the folding of the band structure into a mini-Brillouin zone can form flat bands, giving rise to the localization of electronic states, and the enhancement of electron-electron interaction leads to a strong light-matter interaction\textsuperscript{5}. Localization-enhanced SHG was therefore observed in these WS\textsubscript{2} spirals.

<table>
<thead>
<tr>
<th>SHG Intensity</th>
<th>Monolayer WS\textsubscript{2}</th>
<th>twisted WS\textsubscript{2} Spirals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>≈ 0°</td>
<td>13°</td>
</tr>
<tr>
<td>Absolute Intensity (a.u.)</td>
<td>386</td>
<td>Max.-Min. 52464 – 4720</td>
</tr>
<tr>
<td>Intensity Ratio ((I_{\text{Spirals}}/I_{\text{Monolayer}}))</td>
<td>Max.-Min. 136 – 12</td>
<td>Max.-Min. 16045 – 3702</td>
</tr>
</tbody>
</table>

Table 1  
The SHG absolute intensity and SHG intensity rate of monolayer WS\textsubscript{2} and twisted WS\textsubscript{2} spirals with twisted angle at 0.1°, 13°, 16° and 20°

We further analyzed the effect of local inversion symmetry on the SHG of the stacked WS\textsubscript{2} spirals. Jiang \textit{et al.} found that the bilayers MoS\textsubscript{2} with a twisted angle of 0° show increased SHG intensity with increasing layer number due to broken inversion symmetry, while MoS\textsubscript{2} with 60° bilayers showed no SHG because of local inversion symmetry\textsuperscript{32}. Figure 3 shows the representative analysis of two different cases, namely the stacked WS\textsubscript{2} (Fig. 3a-d) and the spiral WS\textsubscript{2} (Fig. 3e-h). In the first three cases of stacked WS\textsubscript{2}, the inversion symmetry is broken and thus SHG is generated. However, when stacked to the fourth layer, the angle between layers 1 and layer 4 is 60°. The inversion symmetry is then recovered, resulting a reduced overall SHG. In addition, Hsu \textit{et al.} found that twisted angles of 2°, 16°, 30°, and 37° all resulted in an enhancement of the SHG intensity in the stacked region with respect to monolayer WS\textsubscript{2}\textsuperscript{33}. However, when the twisted angle is 54°, the SHG intensity is smaller than that of monolayer MoS\textsubscript{2}, suggesting that the SHG of twisted bilayer MoS\textsubscript{2} is a coherent superposition of SHG fields from individual layers\textsuperscript{34}. The SHG of a 2H phase hexagonal WS\textsubscript{2} spiral was also examined, and the results are shown in Fig. S9. The angle between two screw dislocations of the hexagonal spiral WS\textsubscript{2} is 60° (Fig. S9c), resulting in the alternating structure of the lattice with broken inversion symmetry in odd
layers and inversion symmetry in even layers\textsuperscript{35}. Figure S9d confirms that the SHG signal appears only in odd layers, suggesting a strong dependence on inversion symmetry.

Next, the variation of the SHG signal in the supertwisted WS\textsubscript{2} spiral is explained as follows. Given $\alpha = 20^\circ$ (Fig. 3a-d and 3e-h corresponding to multilayer and supertwisted WS\textsubscript{2} structures), the twisted angle between the first two layers is 20° and between Layer 1 and Layer 3 is 40° (Fig. 3f, 3g). They all exhibit broken inversion symmetry, resulting in increased SHG intensity with layer numbers. In contrast, as the twisted layer increases toward the fourth layer, the twisted angle relative to the first layer is 60° (Fig. 3d, 3h). The inversion symmetry between Layer 1 and Layer 4 is then restored, and the SHG is expected to be fully quenched. However, since the fourth layer maintains a twist angle of 40° and 20° relative to the second and third layers, respectively, the SHG intensity of the fourth layer would not decrease to zero. In a similar case, the inversion symmetry between Layer 2 and Layer 5 leads to a reduced SHG when rotating to the fifth layer (Fig. S10). In short, the twisted angle between low-number layers in a supertwisted spiral WS\textsubscript{2} is not 60°, resulting in broken inversion symmetry. This allows the SHG field of each layer to be coherently superimposed, leading to an increased SHG intensity with increasing layer number. On the contrary, the high-number layers may suffer from the SHG quenching effect due to the inversion symmetry between certain layers with a specific twisted angle. Although the SHG intensity mainly depends on the inversion symmetry broken of the crystal structure, the interaction between light and matter will be affected by strain\textsuperscript{36} and the moiré potential\textsuperscript{37}. Remarkably, simple optical spectroscopy experiments can provide information on strain and lattice distortions in moiré crystal with nanometer-sized supercells.

**Layer-dependent optical spectroscopy**

We recorded the PL spectra from different layers of the supertwisted WS\textsubscript{2} spirals to investigate the role of moiré potentials during light-matter interaction. Typical layer-dependent PL spectra from a supertwisted WS\textsubscript{2} spiral with $\alpha = 13^\circ$ (inset) are shown in Fig. 4a. As the number of layers increases, the PL peak first shows a slight redshift and then a strong blueshift (Fig. 4b). Previous studies have shown that the WS\textsubscript{2} monolayer has a direct bandgap of 1.96 eV ($\sim$ 643 nm), while the WS\textsubscript{2} multilayer has an indirect bandgap\textsuperscript{38,39}. In addition, as the layer number increases, the PL peak position tends to shift to the longer wavelengths and the PL intensity decreases rapidly. Note that the peak position of Region 1 (the bottom layer) is around 665 nm (Fig. 4b), which is longer than that of the WS\textsubscript{2} monolayer. This indicates that Region 1 is not a WS\textsubscript{2} monolayer. This makes sense since the supertwisted WS\textsubscript{2} spiral was grown on the self-constructed ribbons composed of single or multiple-layer WS\textsubscript{2}, but not on the Si/SiO\textsubscript{2} substrate. Therefore, the bottom layer of the supertwisted WS\textsubscript{2} spiral consists of stacked multilayer WS\textsubscript{2}, which has an indirect bandgap.

The PL intensity increases slightly from Region 1 to Region 5, and then decreases rapidly after Region 5 (Fig. 4b). Previous work has shown that the supertwisted WS\textsubscript{2} spiral has a triangular distortion due to an additional protrusion on substrates, and thus introduces additional tensile strain\textsuperscript{21}. The observed slight
PL redshift is due to the increased tensile strain caused by the continuous growth of the twisted WS\(_2\) layer, resulting in a reduced bandgap energy. Compared to the bottom WS\(_2\) layer, the strain in the middle WS\(_2\) layers is enhanced significantly due to localization, leading to a PL redshift and an increase of the PL intensity\(^{40,41}\). However, the top layer is expected to have a lower strain than the middle layers, making it an indirect band gap semiconductor with blue-shifted PL spectra\(^{42}\). Furthermore, the layer-dependence PL spectra of other supertwisted WS\(_2\) spiral with twisted angle of 16° (Fig. S11) and 19° (Fig. S12) also confirm the existence of moiré potentials. These results suggest that the electronic band structure of WS\(_2\) is modified by the twisted angles, leading to the possibility of flat bands with localized states and enhanced electronics correlation\(^{33}\). Although the peak position shifts as a function of band gap are illustrated nearly the same for all supertwisted WS\(_2\) spiral with different twisted angles. The similar PL peak positions in different twisted angles structures are characteristic of exciton trapped in a moiré potential. This is mainly because the moiré exciton-related photoluminescence dose not exhibit distinct characteristic peaks at room temperature\(^2,4\).

In order to analyze the effect of the strain and the moiré potentials on the lattice vibration mode, we measured the Raman spectra of different regions\(^{43,44}\). Here we focus on the A\(_{1g}\) and E\(_{2g}\) Raman modes of the supertwisted WS\(_2\) spirals. The A\(_{1g}\) peak at about 420 cm\(^{-1}\) represents the out-of-plane phonon mode due to the intralayer vdW restoring force\(^{45}\), the E\(_{2g}\) peak at around 350 cm\(^{-1}\) corresponds to the in-plane phonon modes indicating the long-term Coulomb interaction\(^{45}\). Figure 4c shows the Raman spectra recorded from different regions of the supertwisted WS\(_2\) spiral with a twisted angle of 13°. Their peak positions are extracted and then plotted as a function of region number in Fig. 4d. The A\(_{1g}\) mode shows a significant blueshift with increasing layer number, indicating a reduced vdW gap and increased vdW interaction\(^{44}\), resulting in the enhanced restoring force of the interlayer molecular vibrations and lattice stiffen. The E\(_{2g}\) mode shows a blueshift with increasing layer number, which is different from previous Raman results of MX\(_2\) materials\(^{44}\). Generally, the A\(_{1g}\) peak position of multilayer WS\(_2\) with twisted angles from 0° to 60° shows a blueshift, while the E\(_{2g}\) peak position shows a redshift due to an enhanced dielectric-screening-related long-range Coulomb interaction. This means that the 0° and 60° stack has the strongest interlayer coupling, while the other angles have a weaker coupling\(^{44,45}\). Similar results were also observed in multilayer AA stacked WS\(_2\)^{36}. Given these considerations, the observed E\(_{2g}\) blueshift in supertwisted WS\(_2\) spiral could be due to the weakening of the long-range Coulomb interactions caused by interlayer twisting. These twists increase the effective restoring force of the atoms in the layers and thus enhance the vibrations.

To verify that we observed a moiré potential and strain phenomenon, we carried out the layer-dependent Raman spectra of the different twisted angles (\(\alpha = 13°, 16°\) and 19°). It was found that the A\(_{1g}\) and E\(_{2g}\) peak position of the supertwisted WS\(_2\) spiral make no difference affected by the twisted angle, as show in Fig. S11 and S12. This is because the substrate is not atomically smooth, each layer introduces additional tensile strain, with the lower layer accumulating more strain than the upper layer\(^{36}\) and also the
effect of thermal expansion mismatch of WS$_2$ and SiO$_2$. Consequently, the vdW interactions and the interlayer coupling in the supertwisted WS$_2$ spiral are weakened, while the long-range Coulomb interaction between layers is weakened.

Our spectroscopic measurements highlight the existence of the moiré potential in supertwisted WS$_2$ spirals originating from the moiré lattices. As twisted angle changes, the folding of the band structure into a mini-Brillouin zone can form flat bands, giving rise to the localization of electronic states and the enhancement of electron-electron interaction. Furthermore, the localization pattern of the flat band can be tuned by the twisted angle and is determined by the atomic relaxation in the moiré pattern. Last, gate-tunable experiments are expected to reveal the phenomenology of correlated states in this supertwisted spiral WS$_2$.

Conclusions

In summary, we found that the twisted WS$_2$ spirals with different twisted angles can be grown on Euclidean or non-Euclidean surfaces using a one-step water-assisted chemical vapor deposition. The local SHG signals in these spirals can be amplified up to 36–136 times depending on their twisted angles, indicating a strong light-matter interaction. The spectroscopic measurements in these spirals suggest a continuous and subtle evolution of atomic configuration. The inversion symmetry is modified as the twisted angle changes, leading to a faster increase in SHG intensity of the supertwisted spirals with smaller twisted angles. In a certain range of small twisted angles ($\approx 0^\circ$), a maximum SHG enhancement was observed with increasing layer number, which originates from the broken inversion symmetry and the moiré potential. The layer-dependent PL and Raman spectra highlight the existence of moiré potentials in twisted WS$_2$ spirals. Our work implies that the twisted WS$_2$ spirals could provide an attractive platform for the study of light-matter interactions and many-body effects. In the near future, gate-tunable experiments could reveal the phenomenology of correlated states in these systems, such as topological insulating states, when the flat bands are tuned to be partially filled.

Materials and Methods

Water vapor-assisted chemical vapor deposition growth of WS$_2$ spirals

The supertwisted WS$_2$ spirals were synthesized by water vapor-assisted chemical vapor deposition on a silicon wafer covered with 280 nm SiO$_2$. WS$_2$ powder in a quartz boat was placed at the heating center of a quartz tube in the CVD setup. 0.5–1 ml deionized water was placed upstream outside the heating preservation zone as the water vapor source. The substrates were placed about 6–8 cm downstream (700–800°C) of the quartz tube. A high purity argon flow rate of 80 sccm was introduced into the CVD system for 40 min to discharge the oxygen inside the tube before heating. Then, the furnace was heated...
to 1150°C in 35–40 min with an argon flow of 80 sccm and maintained at this temperature for 15–25 min for spiral WS$_2$ growth.

**Material characterizations**

The surface morphology of spiral WS$_2$ was characterized by optical microscopy (Zeiss Axio Imager A1) and atomic force microscopy (AFM Bruker Multimode 8-HR). AFM probe model used Scanasyst-AIR with $f_0 = 70$ kHz $k = 0.4$ N/m $T = 650$ nm $L = 115$ µm and $W = 25$ µm.

SHG measurements were performed using a self-assembled confocal microscope in reflection geometry and a Ti:Sapphire laser (Chameleon Ultra) at 800 nm. The laser was vertically incident on the spiral WS$_2$. A 100× microscope objective (Olympus, NA = 0.9) was used to collect reflection light. The SHG signals through a short-pass filter (Thorlabs, cut-off wavelength: 532 nm) were recorded by a charge-coupled device (CCD). The size of the laser spot was 2 µm, and power was 84 mW/cm$^2$.

Raman and PL spectroscopy of the spiral WS$_2$ were measured at room temperature using a confocal microscope (WITec, alpha-300) with 532 nm laser light. The laser was focused onto the sample with a 100× objective (NA = 0.9). Raman spectroscopy used a raster of 1800 g/mm and a cycle time 1 s, at an excitation laser power of 2 mW/cm$^2$. The PL spectra were measured using a raster of 300 g/mm and cycle time 1 s, and excitation laser power of 2 mW/cm$^2$.

**Declarations**

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**Author contributions**

The project was designed and managed by X.P.F.. The samples were synthesized and characterized by Q.W, T.T.. Raman and PL measurements were performed by Q.W, T.T, R.J.C, X.C.W.. AFM measurements were provided by T.T, X.P.F.. SHG measurements were obtained by T.T, and Y.Y.. Interpretation of data was provided by X.PF, J.Y.X, Y.Z.Z, Q.J.S, J.C, Z.Y.G, H.Y. W, Y.Y. H.. X.PF, J.Y.X, Y.Z.Z revised the manuscript. All authors reviewed and contributed the revision of the manuscript.

†Q.W and T.T. contributed equally to this work.
Conflict of interest

The authors declare no competing interest.

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**Figures**
Figure 1

**twisted spiral WS$_2$ with different twisted angles.** a, b Optical and AFM image of the twisted spiral WS$_2$. c-f Optical and AFM images of the left-handed and right-handed supertwisted spiral WS$_2$, respectively. The red dashed lines mark the edge of the WS$_2$ ribbons. Inset in (d) shows the height profile of the ribbon. g
Structural model of the supertwisted spiral WS$_2$ with different left-handed and right-handed twisted angles.

**Figure 2**

**Angle-dependent SHG of twist spiral WS$_2$.**  
(a) Optical image of the twisted spiral WS$_2$ and layer-dependent SHG.  
(b, c) Optical image of the supertwisted spiral WS$_2$ with $\alpha=13^\circ$(d), $\alpha=16^\circ$(g) and $\alpha=20^\circ$(j), and
their layer-dependent SHG \((e, f), (h, i), (k, l)\), respectively. The colored crosses in these figures show the region where SHG signals are collected. The larger the region number, the thicker the layer.

**Figure 3**

**Effect of inversion symmetry on the variation of supertwisted spiral WS\(_2\) SHG.** Schematic drawing of the stacked bilayer WS\(_2\) with \(\alpha=0^\circ\) (a), \(\alpha=20^\circ\) (b), the stacked tri-layer (c) and four-layer (d) WS\(_2\) with \(\alpha=20^\circ\). The twist angle is 40° between the first and third layers of the stacked tri-layer WS\(_2\) (c) and 60° between the first and fourth layers of the stacked four-layer WS\(_2\) (d). (a-c) have broken inversion symmetry while (d) shows inversion symmetry in their interlayers. e Bilayer structure model of the aligned spiral WS\(_2\). Schematic sketches of the supertwist spiral bilayer WS\(_2\) with \(\alpha=20^\circ\) (f), trilayer WS\(_2\) with \(\alpha=20^\circ\) (g), and four-layer WS\(_2\) with \(\alpha=20^\circ\) (h), driven by a screw dislocation of \(\alpha=20^\circ\). The twist angle is 40° between the first and third layers of the supertwist spiral tri-layer WS\(_2\) (g) and 60° between the first and fourth layers of the supertwist spiral four-layer WS\(_2\) (h). (e-g) have broken inversion symmetry while (h) shows inversion symmetry in their interlayers.
Figure 4

Layer-dependent PL and Raman spectra. a PL spectra recorded from different layers of a supertwisted spiral WS₂ (13°), marked with crosses in the inset of panel (b). b PL peak positions (top) and intensity (bottom) as a function of layer number derived from (a). The PL peak position has a slight redshift before a significant blueshift, the PL intensity increases slightly before decreases sharply. The inset is the optical image of the tested material. c Raman spectra recorded from different layers of the supertwisted spiral
WS$_2$ in the inset of (b). d Peak position of E$_{2g}^{\frac{1}{2}}$ (bottom) and A$_{1g}$ (top) versus layer number, a continuous blueshift is observed.

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