Doubly-Resonant Enhancement of Second Harmonic Generation from a WS$_2$ Nanomesh Polymorph with a Modified Energy Landscape

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Although transition metal dichalcogenides (TMDs, e.g., WS$_2$, WSe$_2$, MoS$_2$, MoSe$_2$) have emerged as highly promising 2D materials for nonlinear optics, they are limited by intrinsically small light-matter interaction length and (typically) flat-lying geometries. The first hyperspectral multiphoton analysis of a tridimensional webbed network of densely-packed stacks (of 1–5 layers) of twisted and/or fused 2D nanosheets of WS$_2$, referred to as “nanomesh”, is presented here. The optical second harmonic generation (SHG) is mapped across the three characteristic spectral features (A, B, and C) and two-photon luminescence and third harmonic generation signatures are established. Compared to flat-lying WS$_2$ layers, the nanomesh is highly efficient, broadband, and robust against degradation (with main enhancement originating from the C feature, spreading from 850 to 1100 nm), and scalable in terms of growth. The origin of these spectral differences is assigned to hotspots, whose location changes depending on the wavelength of illumination. The main SHG enhancements result from double resonances in an energy landscape modified by in-built defects (e.g., vacancies and their passivated variants, or grain boundaries) that induce intra-bandgap energy levels. These characteristics establish the nanomesh as a prime candidate for integration into quantum optical technologies, such as miniaturized devices on chip.

1. Introduction

Nonlinear optics has essential applications in optical amplification,[1] optical switches,[2,3] modulators,[2,3] ultrafast pulse laser generation,[4,5] sensors,[6] advanced spectroscopy,[7] high-resolution imaging,[8] and materials analysis.[9] Second harmonic generation (SHG), being the first term in the nonlinear optical expansion is often the largest. It is an exquisitely symmetry-sensitive nonlinear optical process. SHG can therefore be used to characterize symmetry-breaking effects, including but not limited to: externally applied magnetic[10] and electric fields,[11] chirality,[12] strain,[13] localized surface electric fields,[14] and surface roughness[15] with thickness down to atomic monolayers. When it comes to SHG applications, commercial nonlinear mediums are usually mm-thick bulk crystals (lithium iodate [LiIO$_3$], beta barium borate [BBO], and potassium titanyl phosphate [KTP], to name a few). Therefore, a material that has the possibility for miniaturization, scalability, strong nonlinearity, high-damage threshold, broadband, and efficiency is required for electronic devices and on-chip integration.[16]

Following the discovery of graphene,[17] a whole class of atomically-thin materials with unusual optical and electronic properties have emerged—the so called two-dimensional (2D) materials. Among these, transition metal dichalcogenides...
(TMDs) offer a remarkably tunable bandgap structure— with decreasing thickness the bandgap of most TMDs transitions from indirect to direct.\textsuperscript{[18]} As a result, TMD materials exhibit highly tunable, thickness-dependent linear and nonlinear optical properties.\textsuperscript{[19]} SHG studies of TMD flakes/sheets (monolayers and van der Waals bonded multilayers of typically 1–10 layers) have been reported for WS\textsubscript{2},\textsuperscript{[20–22]} WSe\textsubscript{2},\textsuperscript{[23–26]} MoS\textsubscript{2},\textsuperscript{[27–33]} MoSe\textsubscript{2},\textsuperscript{[34]} MoTe\textsubscript{2},\textsuperscript{[35]} as well as for MoS\textsubscript{2}-WS\textsubscript{2} and MoS\textsubscript{2}-WSe\textsubscript{2} heterostructures.\textsuperscript{[36]} Huge SHG responses were reported\textsuperscript{[19]} (≈10\textsuperscript{5} times more in BBO and KTP,\textsuperscript{[37]} and ≈10\textsuperscript{6} more than in bulk TMDs).\textsuperscript{[38]} However, although these TMD flakes/sheets provide a strong non-linear conversion efficiency per unit thickness, the intrinsically small light-matter interaction length constitutes a substantial limiting factor. Moreover, they have a strong wavelength dependence (due to the bandgap) that restrains their applicability.

In order to increase the light-matter interaction length, 2D materials can be assembled into complex tridimensional structures, using liquid crystal technology,\textsuperscript{[39,40]} surface tension,\textsuperscript{[41–43]} or electrochemical assembly.\textsuperscript{[44]} Other promising tri-dimensional (3D) assemblies include the synthesis of 3D tubular MoS\textsubscript{2} architectures,\textsuperscript{[45]} nanofilms of vertically aligned MoS\textsubscript{2} and WSe\textsubscript{2} materials,\textsuperscript{[46]} nanoporous double-gyroid MoS\textsubscript{2} networks or vertically standing MoS\textsubscript{2} and HFS\textsubscript{3}.\textsuperscript{[47,48]}

So far, the nonlinear optical properties of 3D assemblies of 2D materials have only been touched upon. For instance, we introduced a material that consists of 2D nano-sheets randomly arranged in densely-spaced, tridimensional networks—designated as WS\textsubscript{2} nanomesh.\textsuperscript{[49]} We noticed that this nanomesh appears to have intriguing and strong SHG properties but they were evaluated at a single wavelength and the origin of the signal was not investigated. Also, J. Zhang et al. reported SHG enhancement from vertical MoS\textsubscript{2} nanosheets.\textsuperscript{[50]} They studied only two excitation wavelengths, the origin of the signal was not examined and the reason for the enhancement was attributed simply to an increase of material thickness.

Here, we present the first hyperspectral multiphoton analysis of a 3D network of 2D sheets—the nanomesh. We map the SHG across all three (A, B, and C) spectral features and we evaluate their two-photon luminescence (TPL) and third harmonic generation (THG). We reveal that the nanomesh presents very different multiphoton spectral signatures from those of flat-lying WS\textsubscript{2} multilayers. We pinpoint the origin of these differences to three types of defect locations (hotspots) with very distinctive spectral properties—their location depends on the wavelength of illumination. This behavior has direct consequences for the SHG enhancement and its spectral bandwidth, both of which are key parameters for applications. Two benchmarks are presented for the SHG enhancement: z-cut quartz and flat-lying WS\textsubscript{2} multilayers. Compared to a z-cut quartz surface, the nanomesh is 9.05 × 10\textsuperscript{4} times more SHG active and could be even more (up to 1.76 × 10\textsuperscript{5} times the z-cut quartz’ response). Although we were not able to directly measure the SHG response of a substrate-supported monolayer, we have successfully measured that of 2-, 3-, 4- and 5 substrate-supported layers. From these data and from the relevant literature values,\textsuperscript{[20,21]} we estimate the SHG response of a monolayer and compare it to that of the nanomesh. We find that the nanomesh is ≈17.8 times more SHG active (when spatially averaged) than an individual mono-layer, and that it could be increased up to a limit of ≈35 times that of the monolayer. The large SHG signal can be attributed to the presence of numerous mid- and intra-bandgap defects that are clearly visible in the linear optical spectra of our materials, at half the energy and twice the wavelength of the A, B (excitonic transitions) and the C (multiple transitions) TMD spectral features. These defects result in doubly-resonant SHG enhancements, see Figure 1a. Additionally, the SHG response in the nanomesh is broadband, which makes it robust against degradation; it is mostly occurring at the intrinsically broader C spectral feature and strong enhancement extends over 250 nm in the spectral range (850–1100 nm). We demonstrate that the SHG response in the nanomesh originates mainly from the density and distinct spectral properties of clearly pronounced hotspots.

2. Experimental Section

The non-linear optical properties of all the above mentioned WS\textsubscript{2} materials (tridimensional nanomesh and flat-lying multilayers) were investigated through hyperspectral multiphoton microscopy. The 2H coordination and stacking of these materials were established by Raman spectroscopy.\textsuperscript{[49]} All samples were illuminated from 850 to 1300 nm, in increments of 25 nm with constant average power of 0.5 mW (except for the two points at 900 and 925 nm that were excluded due to instrument limitation). For each incident wavelength, an emission spectrum was recorded (from 425 to 650 nm, in 32 steps). Multiphoton emission intensity was quantified by using the grayscale pixel values (0 to 255). For more details on the experimental configuration see Figure S1, Supporting Information.

The nanomesh is schematically shown in Figure 1b as an extended 3D network of 2D sheets. Figure 1c shows scanning electron microscopy (SEM) images of the nanomesh, which clearly reveal a densely-packed, randomly arranged, tridimensional network. To achieve this network configuration, the 2D sheets initially nucleated at the apexes of nanotubes or grew by epitaxy on their sides, then merged with the opened and exfoliated nanotubes to finally yield a 2D phase material made of nanotomicro scale webbed and interconnected 2D sheets.\textsuperscript{[49]} Such sheets can be seen in Figure 1d that shows transmission electron microscopy (TEM) images of the nanomesh. The TEM on the left demonstrates Moiré patterns resulting from WS\textsubscript{2} sheets twisted in respect to each other. The TEM on the right shows sheets that are stacked and twisted by a small angle (< 60°), see also Figure S2, Supporting Information. Such 2D twisted sheets resulted from their specific growth process from WS\textsubscript{2} nanotubes filled with sub-oxide precursor material. Figure 1e shows the nanotubes polymorph phase that is a “precursor” to forming the nanomesh.\textsuperscript{[49]} A third polymorph phase can be referred to as “intermediate,” where 2D sheets coexisted with a substantial amount of nanotube (one-dimensional (1D)) phase.

For reference, flat-lying, substrate-supported WS\textsubscript{2} multilayer sheets were produced (grown by chemical vapour deposition (CVD) under conditions similar to ref. \textsuperscript{[51]} see Supporting Information) that are shown in Figure 1f. The image corresponds to bright field reflection microscopy, where each multi-layer sheet can be seen as a green triangle/polygon. Each shade of green corresponds to a different number of layers: bilayer (2L), trilayer (3L),...
Figure 1. Second harmonic generation (SHG) processes and characteristics of the materials (nanomesh and benchmarks). a) Schematic diagram illustrating non-resonant, resonant, and doubly-resonant SHG processes. In the energy diagram, A and B are spectral features at the K points of the Brillouin zone and C represents spectral features near the Γ points. 2A, 2B, and 2C are spectral lines at twice the A, B, and C wavelengths, respectively. b) Schematic diagram of the nanomesh network. c) Scanning electron microscopy (SEM) image of the WS₂ nanomesh at two different scales. d) Transmission Electron Microscopy (TEM) from the nanomesh. The TEM on the left reveals Moiré patterns from as-grown, twisted WS₂ sheets. The TEM on the right reveals stacks of twisted WS₂ sheets with low twist angles. e) SEM of nanotubes—a WS₂ polymorph material from which the nanomesh evolves. f) Optical micrograph of the different WS₂ multilayers. The number of layers present is represented by #L. g) Reflectivity spectra obtained in bright-field microscopy at normal incidence with unpolarized light, from three related WS₂ polymorphs: nanotubes, nanomesh, and an intermediate phase. The six spectral features from (a) are indicated with vertical lines in (g).

In each case, the uniform color indicates homogeneous and consistent thickness.

Linear optical reflection spectra from the three WS₂ polymorph phases are presented in Figure 1g, for both the visible and the near infrared wavelengths. The characteristic A, B, and C spectral features in the visible are clearly noticeable; as the samples absorbed more light at these wavelengths there is less reflection. In addition, further spectral features can be seen in the near infrared, approximately at the 2A, 2B, and 2C wavelengths, evidencing the strong presence of intra- and mid-bandgap energy levels. Such spectral features highlight the modified energy landscape in the intra-gap region for these new polymorph phases. Photoluminescence results comparing emission at the A, B, and C spectral lines from the nanomesh and the flat-lying films are provided in Figures S3 and S4. Supporting Information: the nanomesh shows a very large response at the C feature, that is entirely absent in the flat-lying films; this is also accompanied by a broadened spectral response at the A and B features for the nanomesh.

3. Enhanced SHG Intensity and Distinct SHG Emission Spectrum from the Nanomesh

A schematic diagram of the multiphoton measurements is shown in Figure 2a. Measurements of the SHG and THG from our samples are shown in Figure 2b. The layer thickness of the flat-lying multilayers is estimated by reflection microscopy and nonlinear optical microscopy. The SHG dependence on layer thickness is characteristic of the TMD’s crystal order. TMD crystals usually present three types of coordination structures and stacking orders, they are known as the 1-trigonal (1T), 2-hexagonal (2H), and 3-rhombohedral (3R) phases.
The 2H phase is semiconducting and it is the most common for mechanical exfoliation and CVD growth; the chalcogens on both sides of the metal atoms align on top of each other, as illustrated in Figure 2a. The 1T phase is metallic and the chalcogens on both sides of the metal atoms do not align. The 3R phase differs from the 2H phase in the order of layer stacking: whereas a 2H bilayer is centrosymmetric, a 3R bilayer is not. Our SHG measurements for 2L, 3L, 4L, and 5L are well in agreement with a 2H WS₂ phase, where SHG is much stronger for the odd-number, non-centrosymmetric multilayers than for even-number, centrosymmetric ones. We were not able to prepare a monolayer, however it has been well established that the SHG intensity from a monolayer of WS₂ is ≈2 times that of the trilayer (3L). The authors measured at 800 nm, which is close to our own measurements at 875 nm. An estimate of the monolayer SHG is therefore included in Figure 2b as a grey square symbol. Figure 2b clearly demonstrates a dramatic difference in SHG emission from the two types of samples—the signal from the nanomesh phase is much larger than that of the flat-lying multilayers (and that of the estimated value for the monolayer). Specifically, in the nanomesh phase, the normalized (to 255) surface-average SHG intensity is 126.7, which is 9.05 × 10⁴ times more than the surface-average SHG response from a reference z-cut quartz, that is, 0.014. In the nanomesh, SHG originates from well-defined emission hotspots. The hotspot-averaged SHG reaches 246.4, which is 1.76 × 10⁴ times more than the z-cut quartz. The surface-average SHG emission from the nanomesh can be significantly enhanced by increasing the number of SHG hotspots. In comparison to a WS₂ monolayer (with normalized surface-average SHG intensity of 7.12), we estimate that the surface-average nanomesh SHG is ≈17.8 times larger. By contrast, there is little variation in THG between flat-lying sheets and the three types of out-of-plane polymorphs. Usually, THG in TMDs is weaker than the SHG and this is also what we notice. In Figure 2b, we observe that, starting from the bilayer, the THG increases with the number of layers. This is expected as THG is not restricted by centrosymmetry and increasing the number of layers simply increases the length of light-matter interaction.
Compared to WS$_2$ flat-lying multilayers, the nanomesh presents different multiphoton emission signatures and is much more SHG active. In (a), multiphoton emission spectrum depending on illumination wavelength for the nanomesh. The white dashed lines correspond to the positions of the A, B exciton, and C band-nesting transitions in WS$_2$. The SHG is visible along the diagonal line. The largest SHG enhancement is observed at the C spectral feature. The lower panel reveals the lowest intensity signals, close to the detection limit of the experiment. In (b–e), the maps represent multiphoton emission spectra depending on illumination wavelength for 2L (bilayer), 3L (trilayer), 4L, and 5L respectively. In (b), a clear two-photon luminescence (TPL) signal is observed. In all multilayers, the largest SHG enhancement is observed at the Aspectral feature.

A comparison with any of the flat-lying multilayers in Figure 3b–e immediately reveals that the SHG spectral profile of the nanomesh is very different. The specific details and an analysis of these flat-lying multilayers are provided in the Supporting Information (Figures S5 and S6, Supporting Information). In all the flat-lying WS$_2$ sheets, the SHG is strongest at the resonantly enhanced A spectral feature. The SHG signal is clearly visible as a diagonal line and TPL can be observed in the bilayer, indicating the presence of an exciton energy level. As expected, the SHG signal is much stronger in the 3L and 5L flakes, compared to the 2L and 4L flakes. Unfortunately, due to instrument limitations, we were unable to measure the sample at 900 and 925 nm illumination. Nevertheless, in all figures (Figure 3b–e), a low-level SHG signal can be observed very near the C energy/wavelength (at 875 nm). We note that in comparing SHG intensities from flat-lying multilayers to the nanomesh, the orientation angle of the multilayers can play a significant role, but in our experiments, this is not the case due to the absence of an analyzer, see Figure S7, Supporting Information.

For further comparison, the multiphoton signatures of all three polymorph phases (nanotubes, 1D and 2D mixed phase, and nanomesh) have been investigated and are presented in Figure S8, Supporting Information: they all show similar spectral features marking their common origin (as these phases evolve from each other), with the nanomesh giving the strongest signals. At 875 nm illumination (corresponding to the C feature), the SHG emission from the nanomesh is ≈35 times larger than that of the trilayers. Additionally, Figure S9, Supporting Information presents a direct comparison of the SHG intensity from all samples that we investigated (polymorphs and flat-lying multilayers). The figure clearly demonstrates that the SHG intensity from the polymorphs is much larger than that of the 2H WS$_2$ flat-lying multilayers, across a wide wavelength range.

There is evidence in the literature that defects can cause intra- and mid-bandgap energy levels that in turn can result in doubly-resonant SHG. Using CVD-grown polygonal flat-lying sheets of mono- and few-layer WS$_2$, it was shown that defect regions can lead to double resonant SHG enhancement compared to un-defected regions of material. Significant SHG enhancement factors were recorded between defected and un-defected monolayer regions, and S vacancies creating mid-bandgap states were invoked as the most likely types of defects in these cases. S-vacancies are not chemically stable in the atmosphere, however intra- and mid-bandgap energy states can occur for passivated vacancies as well. Indeed, mid-bandgap energy levels have been reported for S vacancies in WS$_2$, for hydrogen passivated S vacancies in MoS$_2$, and for oxygen passivated Mo defects in MoSe$_2$. Additionally, defects broaden the well-known excitonic A, B, and band-nesting C spectral features of ultra-thin TMDs.

A related defect-induced SHG enhancement mechanism can be invoked, broadly, for our nanomesh material. Here, the defect states are various, structurally and energetically: they can be due to the very large density of sheet edges and sheet grain boundaries (equivalent to extended defects), as well as to the merging with other sheets, present in our nanomesh material. As a result, the SHG intensity does not merely increase proportionally with the number of defects per volume/area, but also changes spectrally as complex intra-bandgap defect bands develop when various defects resulting from multiple S and W vacancies are present. Figure S10, Supporting Information shows TEM of multiple merging sheets where sheet boundaries, that is, lines of extended defects, occur, which is a common characteristic of our material; while Figure S11, Supporting Information of TPL can be observed that is red-shifted with respect to the A feature.

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Information shows atomically resolved edges of sheets, where a high density of various, structural defects are present.

4. SHG Hotspots with Distinct Emission Spectra from the Nanomesh

As stated above, in Figure 3b–e, for all flat-lying multilayer sheets, the maximum SHG emission is observed at the A spectral feature, where it can be attributed to a resonant enhancement of the energy level that is revealed by TPL. In Figure 3a, the SHG peaks at the C spectral feature and it is much weaker at the A feature. Yet, looking at Figure 1g, it is clear that the polymorphs present well-defined mid-bandgap levels for both A and C, suggesting that there should be doubly-resonant SHG at both A-from-2A and C-from-2C. This idea suggests that the SHG spectrum should present peaks at A and B as well, yet it does not. The reason is that defects can differently affect the A and C transitions.

We need to emphasize that contrary to the wide-field microscopy in Figure 1g, the multiphoton microscopy measurements in Figures 3a are performed by scanning a laser beam across the sample surface. The laser spot is an ellipsoid oriented along the direction of light polarization, with major semi-axis of \( \approx 300 \) nm and minor semi-axis of \( \approx 200 \) nm. Therefore, this laser spot probes the spectral response much more locally than wide-field microscopy. Location is important because our polymorphs are not morphologically as simple as the flat-lying sheets are. Whereas Figure 1g shows wide spectral features (including the mid-bandgap features) from the whole (wide-field) illuminated region of the polymorphs, it does not imply that all these features occur together, at all locations on the sample. Depending on the distribution of defects, the local thickness of WS\(_2\), and the local arrangement of layers (e.g., their twist angle with respect to each other) both the local energy landscape and the interaction with light varies. Consequently, different spectral features can be more or less prominent at different locations on the sample surface. Indeed, defects can significantly affect the bandgap, even changing it from direct to indirect,\(^{[65]}\) thereby greatly reducing the TPL (as we observe in our samples).

The A and B spectral features correspond to single energy transitions that are susceptible to small energy band shifts (caused by defects and thickness polydispersion). Such shifts could even cause the resonant SHG to become non-resonant, thereby reducing SHG efficiency. By contrast, the C spectral feature corresponds to multiple energy transitions and is therefore much more robust against small energy band shifts (as one direct energy transition can be replaced by another). As a result, the SHG at the C feature becomes doubly-resonant and greatly enhanced.

The highly local nature of the SHG response is revealed by the SHG microscopy images of the polymorph surfaces in Figure 4.

Figure 4a demonstrates that at the wavelengths corresponding to the A, B, and C spectral features, the nanomesh phase exhibits a collection of well-defined SHG hotspots. These hotspots correspond to clear SHG enhancements for each spectral feature. They occur at different locations, likely due to the random local morphology of the nanomesh network. The density of the SHG hotspots is highest for the C spectral feature, which explains its predominance in the overall response from this sample.

The SHG hotspots are well-defined against the background of the rest of the sample, in all Cartesian directions. Figure 4b presents the coordinate system in Figure 2a, with color-codes for the three, main, orthogonal planes. The plane of the sample is indicated in blue. The red and green planes are perpendicular section cuts through the sample plane. These depth profiles are obtained by performing a series of z-stack images that are later...
assembled for 3D visualization. The z-stack comprised of 43 images taken 0.28 μm from one another, equating to a depth profile of ≈12 μm. As the images indicate, the main hotspot remains bright for a large range of focal plane positions with respect to the sample, that is, the hotspot profile in our images is not significantly affected by refocusing due to chromatic aberration of the objective. Moreover no sample damage could be observed throughout the measurements (see Figure S12, Supporting Information), in agreement with previous reports that TMDs constitute very robust NLO materials, with high laser-induced damage thresholds. [30,66,67]

The nanomesh is not homogeneous at the nano/micro-scale. Different sample regions present distinctive spectral signatures. Doubly-resonant SHG is observed at the three spectral features but in different locations. In each case though, the C-from-2C doubly-resonant SHG is dominant, which explains the overall material SHG response in Figure 2b. Figure 5a shows the SHG response from the nanomesh phase in monochrome greyscale, for illumination at 850 nm (i.e., at the ≈2C spectral feature). The red, green, and blue squares indicate sample regions corresponding to the locations of emission hotspots at A, B, and C (respectively) that have been determined by illumination at 1225, 1050, and 850 nm (respectively). Each square encloses 25 pixels (i.e., an area of ≈0.2 μm²). The squares are spread across the entire sample surface and are all well separated from each other (with a single exception of two overlapping green and red squares, highlighted within a zoomed-in yellow rectangle). For each of these squares, a full multiphoton emission mapping is performed (see Figures S13 and S14, Supporting Information) and the individual SHG intensity spectra are extracted. For each hotspot emission region, that is, for each color of squares in Figure 5a, the SHG spectra are averaged and the results are shown in Figure 5b, together with the standard deviation.

Figure 5b shows three clearly distinguishable doubly-resonant SHG transitions. These transitions are A-from-2A, B-from-2B, and C-from-2C in red triangles, green circles, and blue squares respectively. At 2A, 2B, and 2C, the local maxima clearly correspond to hotspots at A, B, and C, respectively. The distinct profiles of these three spectra demonstrate that the three sets of color-coded sample regions present different local energy properties. However, in all three sets of sample regions, the C-from-2C doubly-resonant SHG transition is clearly dominant, which indicates that defects are inducing mid-bandgap energy levels throughout the sample. The highest SHG intensity we observe was from the set of blue squares (normalized SHG intensity of 246.4). It is indicated with a star symbol and it is this point that is shown in Figure 2b. This value is 1.76 × 10⁴ times more than z-cut quartz. It represents the upper limit of SHG enhancement that can be achieved in this nanomesh sample, that is, for a density of hotspots so high that they cannot be optically resolved. With the current density of hotspots, the SHG enhancement from averaging across the whole sample is 9.05 × 10³ times that of z-cut quartz, which could therefore be up to twice higher. In the green circle and red triangle data sets, the SHG enhancement (combining effects from C-from-2C and B-from-2B) is broadest and reaches ≈250 nm (indicated with a grey double arrow). This value is a lower limit, as it is clear that the 2C spectral feature extends to lower wavelengths, correspondingly extending the broadband response—a spectral region that is unfortunately beyond our experimental capabilities. For reference, the SHG intensity from the regions of lowest SHG intensity (“dark spots”) is provided in Figure S15, Supporting Information.

5. Discussion

SHG enhancement can be due to the symmetry-breaking random arrangement of the nanomesh geometry that can be observed with SEM (Figure 1c). However, such random disorder is not wavelength specific.

For TMD multilayers in the 2H phase the SHG is stronger from an odd number of layers compared to an even number of layers. However, the situation changes once a twist angle is
introduced between the consecutive layers. It has been experimentally observed that in such a case, the SHG intensity scales as a vector sum of the consecutive layers.\[^7,68\] In our nanomesh samples, there are many regions where layers are overlapping at different small (< 60°) stacking angles, see Figure 1d and Figure S2, Supporting Information. These regions are undoubtedly contributing to the SHG enhancement. However, assuming 4 layers (which is toward the upper bound of layers in an individual crystallite),\[^40\] each stacked at the optimal twist angle, the normalized surface-average SHG intensity would only reach 28.48 and this enhancement would account for less than 22.5% of the normalized surface-average SHG intensity (i.e., 126.7 across the entire nanomesh sample). Moreover, the 28.48 from 4 stacked monolayers would account for less than 11.6% of the maximum normalized SHG in the hotspots (246.4). Consequently, while the contribution from a twist angle between consecutive layers is non-negligible, it is likely not dominant in our samples. For reference, in the literature, twists were found to increase the SHG response of substrate-supported bilayers only within single digits.\[^7,69,70\]

Usually, in TMDs the SHG and THG nonlinear optical effects are somewhat limited, as they are mutually exclusive. While monolayers have the strongest SHG response, they also emit the weakest THG. Conversely, the thicker multilayers have larger THG but their SHG is much weaker than that of the monolayer. This limitation is not present in our nanomesh phase that exhibits both stronger SHG than WS\(_2\) monolayers and THG comparable to that from multilayers, see Figure 2b. It has recently been reported that very large nonlinear optical enhancement can be achieved in flat lying TMDs with sum frequency generation (SFG).\[^71\] The maximum SFG intensity obtained by the authors was at 432 nm, when an \(\omega_1\) light pulse at 740 nm (i.e., A exciton) is mixed with an \(\omega_2\) light pulse at 1040 nm (so that \(\omega_1 + \omega_2\) matches a D spectral feature). By comparison, the maximum SHG intensity was shown at 430 nm and it was associated with two light pulses at 860 nm each. This SHG maximum is very close to the 875 nm fundamental wavelength we use as reference here. It can therefore be expected that, in our materials, the SFG enhancement could be even larger than that reported in ref.\[^71\] We emphasize that the nanomesh polymorph provides multiple sources of SHG enhancement, which do not exist in the 2D flat-lying films. These sources are intra-bandgap states arising from in-built sheet-merging regions (Figure S10, Supporting Information), localized defects (Figure S11, Supporting Information), and stacks of twisted sheets (Figure S2, Supporting Information), as well as an overall 3D arrangement that breaks inversion symmetry. While 2D flat-lying films of 3R phase can enhance the SHG response as \(n^2\) with the number of layers \(n,\[^72,73\]\ this enhancement is elicited around the A and B excitonic features. At the broadband C spectral feature, our nanomesh polymorph has a much stronger SHG enhancement than the 2D flat-lying films, whether 2H or 3R; and with still substantial enhancement arising from the A and B features (where the 3R flat-lying films excel). Additionally, compared to 3R stacked materials, the nanomesh is primarily based on the more energetically stable 2H phase. Yet similarly to the symmetry breaking 3R phase, the twisted layers in various stacks of the nanomesh lose their original AB stacking order, hence, breaking inversion symmetry, and couple electronically only via Moiré superstructures. Finally, because it has such a large effective surface area, the nanomesh is ideal for subsequent functionalizations (with molecules, plasmonic nanoparticles, or functional groups that would tune energy states) to modify/amplify their spectral response. Flat-lying films, of any stacking order, only offer their geometric footprint area for functionalization.

6. Conclusion

In summary, although TMDs (such as WS\(_2\)) have emerged as strong NLO materials, their usual 2D arrangements (such as in-plane lying layers) are limiting, because of the intrinsically small light-matter interaction length. A few alternatives have emerged but their nonlinear optical properties have only been touched upon. We present the first full hyperspectral multiphoton analysis of as-grown, out-of-plane, tridimensional networks of densely-packed, randomly arranged WS\(_2\) 2D sheets. We demonstrate that in this nanomesh phase the SHG emission signature is very different from that of flat-lying multilayers. In the nanomesh, the SHG originates from clearly defined hotspots, whose location changes with the wavelength of illumination. In terms of intensity, the surface-average SHG from the nanomesh is \(\approx\)18 times more than that of WS\(_2\) monolayers. It is also 3 to 4 orders of magnitude more than that of a reference z-cut quartz surface. In our nanomesh, at the macro scale, the random tridimensional arrangement of stacked WS\(_2\) sheets constitutes symmetry breaking that is a well-known source of SHG enhancement. The intensity of the SHG could be further increased by increasing the density of such sheets in the nanomesh network, by including plasmonic nanoparticles, and by depositing a second TMD material, whose interfaces with the WS\(_2\) would constitute an additional source of SHG to its intrinsic nonlinearity. In our samples though, the SHG is not only more intense—it presents a distinct spectral shape, with a maximum around the C spectral line. This spectral signature is due to the presence of defects that cause mid- and intra-bandgap energy levels. These energy levels are responsible for a large doubly-resonant SHG enhancement. Moreover, the nanomesh constitutes a more broadband NLO material (up to 250 nm in range), compared to other TMDs because the C spectral feature is intrinsically broader than A and B and because it can be additionally broadened by the defects. The C feature also endows the NLO response of our samples with high robustness against degradation. Highly efficient, broadband, robust and ultra-thin NLO materials (compared to traditional mm-thick crystals) are prime candidates for integration into quantum optical technologies, such as devices on a chip.\[^36\] Our material could be deposited directly at the end of Si waveguides\[^74\] (rather than along their surface\[^43\]) thereby enabling unprecedented miniaturization for these technologies. More targeted bandgap engineering could also produce NLO polymorphs with a doubly-resonant, 2A-2C SHG process that would be suitable for telecom wavelengths.

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
All data supporting this study are openly available from the University of Bath data archive at https://doi.org/10.15125/BATH-00989.

Keywords
2D materials, multiphoton spectroscopy, nonlinear optics, second harmonic generation, transition metal dichalcogenides

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