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# Quantum-sized topological insulators/semimetals enable ultrahigh and broadband saturable absorption†

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Two-dimensional topological insulators/semimetals have recently attracted much attention. However, quantum-sized topological insulators/semimetals with intrinsic characteristics have never been reported before. Herein, we report the high-yield production of topological insulator (*i.e.*, Bi<sub>2</sub>Se<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub>) and semimetal (*i.e.*, TiS<sub>2</sub>) quantum sheets (QSs) with monolayer structures and sub-4 nm lateral sizes. Both linear and nonlinear optical performances of the QSs are investigated. The QS dispersions present remarkable photoluminescence with excitation wavelength-, concentration-, and solvent-dependence. The solution-processed QSs-poly(methyl methacrylate) (PMMA) hybrid thin films demonstrate exceptional nonlinear saturation absorption (NSA). Particularly, Bi<sub>2</sub>Se<sub>3</sub> QSs-PMMA enables record-high NSA performance with a broadband feature. Specifically, the (absolute) modulation depths up to 71.6 and 72.4% and saturation intensities down to 1.52 and 0.49 MW cm<sup>-2</sup> are achieved at 532 and 800 nm, respectively. Such a phenomenal NSA performance would greatly facilitate their applications in mode-locked lasers and related fields.

## 1. Introduction

Two-dimensional (2D) materials have attracted much interest over the past decade due to their fascinating structures and properties.<sup>1,2</sup> Topological insulators (*e.g.*, Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub>, and Sb<sub>2</sub>Te<sub>3</sub>) and semimetals (*e.g.*, TiS<sub>2</sub> and TiSe<sub>2</sub>) are important classes of 2D materials, which have emerged as the new frontiers of materials science.<sup>3,4</sup> Both topological insulators

### New concepts

Topological insulators and semimetals are important classes of 2D materials. Their quantum sheets (QSs) can be treated as extremely quantum-sized topological insulators/semimetals, whose production is highly desired but is far from satisfactory. We herein report the high-yield (> 12 wt%) production of topological insulator (*i.e.*, Bi<sub>2</sub>Se<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub>) and semimetal (*i.e.*, TiS<sub>2</sub>) QSs with monolayer structures and sub-4 nm lateral sizes. The QSs-poly(methyl methacrylate) (PMMA) hybrid thin films demonstrate exceptional nonlinear saturation absorption (NSA). Ultrahigh nonlinear response (72.4 and 68.4%) and ultralow power excitation (0.49 and 0.80 MW cm<sup>-2</sup>) are simultaneously achieved in both Bi<sub>2</sub>Se<sub>3</sub> QSs-PMMA and TiS<sub>2</sub> QSs-PMMA. Such phenomenal NSA performances in quantum-sized topological insulators/semimetals would greatly facilitate their applications in mode-locked lasers and related fields.

and semimetals possess extraordinary properties. The former features a gapless metallic state on their surfaces/edges and insulator characteristics in the bulk,<sup>5</sup> while the latter is characterized by bulk Dirac or Weyl fermions and nontrivial topological surface/edge states.<sup>6</sup> Such unique materials have been widely applied in various fields such as quantum physics,<sup>7</sup> spintronics and magnetoelectronics.<sup>3,6</sup> Compared with bulk layered materials and conventional 2D materials, extremely quantum-sized 2D materials (*e.g.*, 2D quantum sheets (QSs)) demonstrate remarkable performances because of their (both in-plane and out-of-plane) quantum confinement and prominent edge effects.<sup>8</sup> The production of 2D QSs of topological insulators and semimetals is highly desired but far from satisfactory. Fortunately, we have recently developed a general strategy towards the production of 2D QSs and zero-dimensional quantum dots (0D QDs) from their bulk materials.<sup>8-13</sup> However, whether the strategy could be applied for topological insulator and semimetal QS production has never been testified.

Nonlinear optical (NLO) response is the key factor for the evaluation of NLO materials. As a typical third-order NLO effect,

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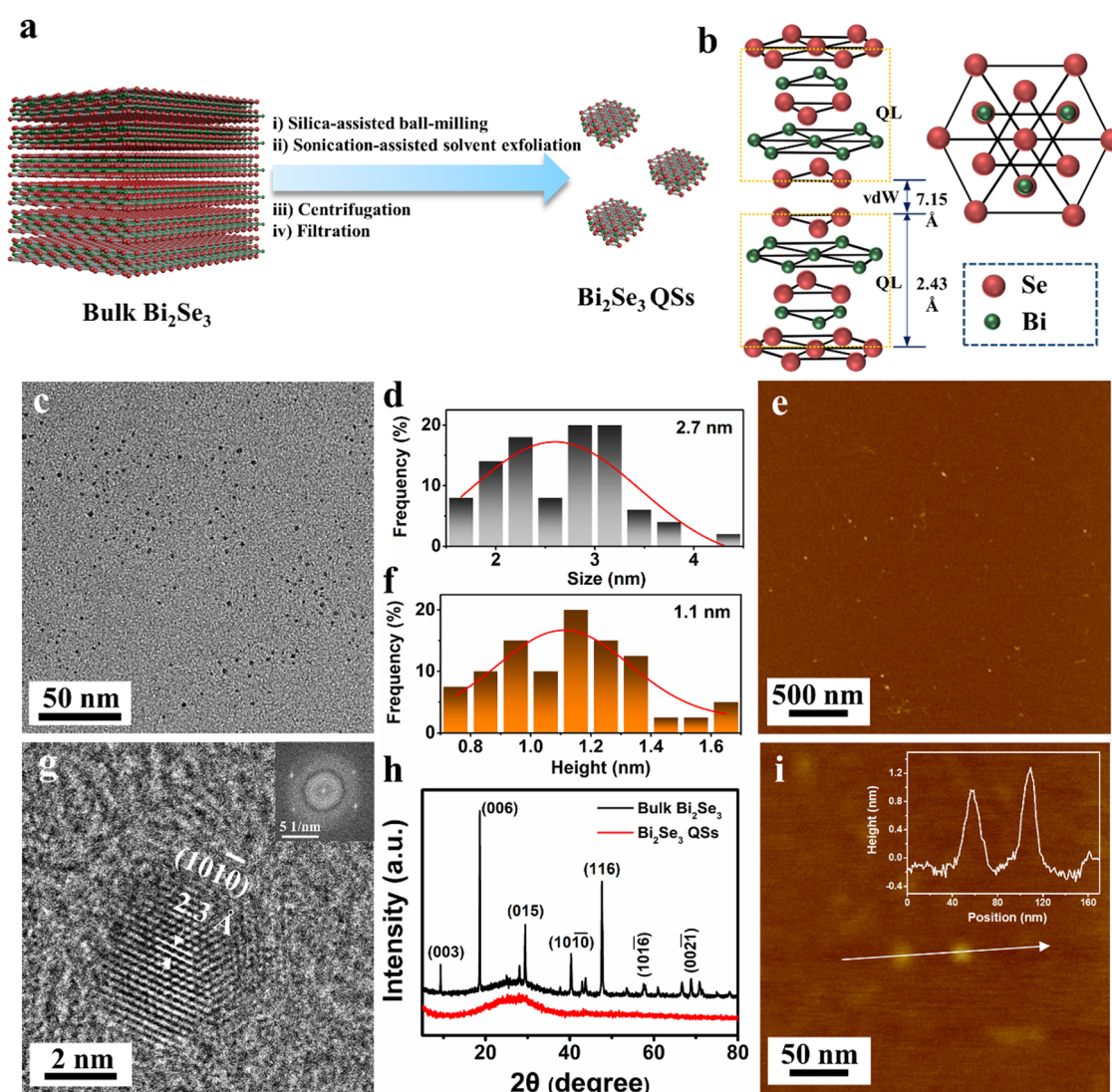
nonlinear saturation absorption (NSA) has attracted growing attention due to their applications in mode-locked lasers and related fields.<sup>14</sup> 2D materials have shown their great potential in NSA by having a deep modulation depth and low saturation intensity.<sup>15</sup> Recently, quantum-sized materials have demonstrated exciting NSA performances.<sup>8–13</sup> Meanwhile, topological insulators and semimetals are interesting candidates for NSA thanks to their unique electronic structures.<sup>16,17</sup> Therefore, quantum-sized topological insulators and semimetals could be very promising in terms of NSA performances.

Herein, we report the successful production of topological insulator (*i.e.*, Bi<sub>2</sub>Se<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub>) and semimetal (*i.e.*, TiS<sub>2</sub>) Qs directly from their bulk materials using an all-physical top-down method. The combination of silica-assisted ball-milling and sonication-assisted solvent exfoliation enabled the high-yield (>12 wt%) production of Qs with monolayer structures

and extremely reduced lateral sizes (<4 nm). The as-produced Qs were structurally intrinsic, which could be determinative to their unique photoluminescence (PL) and NSA performances. The Qs dispersions presented excitation wavelength-, concentration-, and solvent-dependent PL. The Qs-poly(methyl methacrylate) (PMMA) hybrid thin films demonstrated exceptional NSA performances. Particularly, the Bi<sub>2</sub>Se<sub>3</sub> Qs-PMMA realized ultrahigh nonlinear response and ultralow power excitation at wavelengths of 532 and 800 nm.

## 2. Results and discussion

The production process of Bi<sub>2</sub>Se<sub>3</sub> Qs is schematically illustrated in Fig. 1(a), where four sequential procedures: silica-assisted ball-milling, sonication-assisted solvent exfoliation,



**Fig. 1** Scalable production and microscopic characterization of the Bi<sub>2</sub>Se<sub>3</sub> Qs. (a) Schematic illustration of the fabrication process. (b) Schematic diagram of the crystal structure. (c) TEM image. (d) Corresponding lateral size distribution. (e) AFM image. (f) Corresponding height distribution. (g) HRTEM image (inset showing the corresponding FFT pattern). (h) XRD patterns. Data for bulk Bi<sub>2</sub>Se<sub>3</sub> are shown for comparison. (i) High-magnification AFM image (inset showing the corresponding height profile).

centrifugation and filtration were involved.<sup>8</sup>  $\text{Sb}_2\text{Te}_3$  Qs and  $\text{TiS}_2$  Qs were produced by the same method.<sup>8</sup> Excitingly, a single cycle of the production process enabled production of  $\text{Bi}_2\text{Se}_3$  Qs,  $\text{Sb}_2\text{Te}_3$  Qs, and  $\text{TiS}_2$  Qs from their bulk materials ( $> 50 \mu\text{m}$ , Fig. S1a–c, ESI<sup>†</sup>) with extremely high yield of 14.6, 12.1, 15.8 wt%, respectively, suggesting their great potential for future industrialization. No precipitation was observed for the QS redispersions ( $2 \text{ mg mL}^{-1}$ ) when standing still for 7 days under ambient conditions, indicating their long-term stability. Zeta potentials were measured to be  $-22.5$ ,  $-27.6$ ,  $-33.6 \text{ mV}$  for  $\text{Bi}_2\text{Se}_3$  QS,  $\text{Sb}_2\text{Te}_3$  QS, and  $\text{TiS}_2$  QS aqueous redispersions ( $0.1 \text{ mg mL}^{-1}$ ), respectively (Fig. S4, ESI<sup>†</sup>), supporting their satisfactory stability.

The crystal structure of the  $\text{Bi}_2\text{Se}_3$  is schematically illustrated in Fig. 1(b), where the monolayer was constituted by five atomic layers. Multiple microscopic techniques were utilized for characterization of the  $\text{Bi}_2\text{Se}_3$  Qs. Fig. 1 shows the corresponding transmission electron microscopy (TEM) and atomic force microscopy (AFM) images. The microscopic characterization of the  $\text{Sb}_2\text{Te}_3$  Qs and  $\text{TiS}_2$  Qs can be found in Fig. S2 and S3 (ESI<sup>†</sup>). From Fig. 1(c), the  $\text{Bi}_2\text{Se}_3$  Qs with uniform shapes and sizes were obtained. The average lateral sizes of 2.7, 3.2, and 1.9 nm were derived for  $\text{Bi}_2\text{Se}_3$  Qs,  $\text{Sb}_2\text{Te}_3$  Qs, and  $\text{TiS}_2$  Qs, respectively (Fig. 1(d) and Fig. S2, ESI<sup>†</sup>). Fig. 1(g) presents the high-resolution TEM (HRTEM) image and the corresponding fast Fourier transform (FFT) pattern of single  $\text{Bi}_2\text{Se}_3$  Qs, indicating their single-crystalline structures. The lattice spacings of 0.23, 0.24, and 0.21 nm were revealed, corresponding to  $(10\bar{1}0)$ ,  $(10\bar{1}0)$ ,  $(102)$  crystal planes of  $\text{Bi}_2\text{Se}_3$ ,  $\text{Sb}_2\text{Te}_3$ , and  $\text{TiS}_2$ , respectively (Fig. 1(g) and Fig. S2, ESI<sup>†</sup>). The average heights of 1.1, 1.2, and 0.7 nm were derived for  $\text{Bi}_2\text{Se}_3$  Qs,  $\text{Sb}_2\text{Te}_3$  Qs, and  $\text{TiS}_2$  Qs, respectively (Fig. 1(e), (f) and Fig. S3, ESI<sup>†</sup>). The as-produced Qs were monolayers considering that the thicknesses of monolayer  $\text{Bi}_2\text{Se}_3$ ,  $\text{Sb}_2\text{Te}_3$ , and  $\text{TiS}_2$  were approximately 1, 1, and 0.6 nm, respectively.<sup>18–20</sup> Note that the individual height was acquired from the height profile of the single QS (Fig. 1(i)), which was the data source for the statistics in Fig. 1(f). Evidently, all the examined Qs were confirmed as quantum-sized monolayered structures.

Multiple spectroscopic techniques were utilized for further characterization of the as-produced Qs. Fig. 1(h) and Fig. S5 (ESI<sup>†</sup>) show the X-ray diffraction (XRD) patterns of the Qs. From Fig. 1(h), the characteristic peaks at  $9.3$ ,  $18.6$ ,  $29.4$ ,  $40.3$ ,  $47.7$ ,  $57.6$  and  $68.9^\circ$  correspond to  $(003)$ ,  $(006)$ ,  $(015)$ ,  $(10\bar{1}0)$ ,  $(116)$ ,  $(10\bar{1}6)$  and  $(10\bar{2}1)$  crystal planes of  $\text{Bi}_2\text{Se}_3$ .<sup>21</sup> From Fig. S5a (ESI<sup>†</sup>), the characteristic peaks at  $8.7$ ,  $17.4$ ,  $26.3$ ,  $28.2$ ,  $38.3$ ,  $44.6$ ,  $54.2$ ,  $63.2$ , and  $74.8^\circ$  were assigned to  $(003)$ ,  $(006)$ ,  $(009)$ ,  $(015)$ ,  $(10\bar{1}0)$ ,  $(10\bar{1}5)$ ,  $(10\bar{1}8)$ ,  $(10\bar{2}1)$  and  $(10\bar{2}4)$  crystal planes of  $\text{Sb}_2\text{Te}_3$ .<sup>22</sup> From Fig. S5b (ESI<sup>†</sup>), the characteristic peaks at  $15.5$ ,  $31.3$ ,  $34.2$ ,  $44.1$ ,  $47.8$ ,  $53.7$ ,  $57.6$  and  $65.5^\circ$  were indexed to  $(001)$ ,  $(002)$ ,  $(101)$ ,  $(012)$ ,  $(003)$ ,  $(110)$ ,  $(103)$  and  $(004)$  crystal planes of  $1\text{T-TiS}_2$ .<sup>23</sup> Compared with bulk layered materials, the as-produced Qs were identified with significantly reduced crystallinity and extremely enhanced edge states. The Raman spectra of the Qs are shown in Fig. 2(a), (d) and (g), where the insets schematically displayed the typical Raman vibrational modes.

For  $\text{Bi}_2\text{Se}_3$ , as shown in Fig. 2(a), three characteristic peaks were observed in bulk and Qs. The peaks at  $130.5 \text{ cm}^{-1}$  were assigned to  $E_g^2$  modes, whereas the peaks at  $172.7 \text{ cm}^{-1}$  corresponded to  $A_{1g}^2$  modes.<sup>24</sup> Compared with bulk  $\text{Bi}_2\text{Se}_3$ , the  $\text{Bi}_2\text{Se}_3$  Qs showed the  $E_g^2$  modes and  $A_{1g}^2$  modes with lower wavenumbers (*i.e.*,  $128.8$  and  $172.2 \text{ cm}^{-1}$ , respectively), which could be related to the relatively free states of vibrations in quantum-sized  $\text{Bi}_2\text{Se}_3$ .<sup>24</sup> For  $\text{Sb}_2\text{Te}_3$ , as shown in Fig. 2(d), the peaks at  $121.6 \text{ cm}^{-1}$  were assigned to  $E_u^2$  modes, which could be infrared active.<sup>25</sup> The peaks at  $139.3 \text{ cm}^{-1}$  were attributed to the vibrational modes of the Te–Te bonds<sup>26</sup> and the peaks at  $165.7 \text{ cm}^{-1}$  were assigned to the  $A_{1g}^2$  modes.<sup>25</sup> Compared with bulk  $\text{Sb}_2\text{Te}_3$ , the  $\text{Sb}_2\text{Te}_3$  Qs presented greatly suppressed and notably blue-shifted ( $128.7 \text{ cm}^{-1}$ )  $E_u^2$  modes. Such unconventional blue-shift might be caused by the possible change of the topological structure/state (*e.g.*, electronic and vibrational properties) when transforming the bulk into Qs. On the one hand, the quantum confinement effects could alter the topological properties of the as-produced Qs. For instance, the time-reversal symmetry could be disrupted by external perturbations or confinement potentials, resulting in localization of electronic states.<sup>27</sup> On the other hand, the geometric anisotropy of the as-produced Qs could affect the spin–orbit coupling of its surface/edge state, thus modifying the bulk–edge correspondence and the value of the topological invariant.<sup>28</sup> The main reason for the blue-shift in Raman spectra could be attributed to the coupling between surface/edge states and bulk states, as well as the emerging localized states.<sup>29,30</sup> For  $\text{TiS}_2$ , as shown in Fig. 2(g), three characteristic peaks located at  $149.2$ ,  $200.2$ , and  $333.8 \text{ cm}^{-1}$  were assigned to  $E_u$ ,  $E_g$ , and  $A_{1g}$  modes, respectively, consistent with those reported previously.<sup>31</sup> Compared with bulk  $\text{TiS}_2$ , the  $\text{TiS}_2$  Qs demonstrated quite weak  $E_u$  modes at  $147.3 \text{ cm}^{-1}$ . The above-mentioned weakening of Raman signals could be originated from the extremely reduced lateral sizes and layer numbers when tailoring bulk layered materials into their Qs. The constituent elements and chemical states of the as-produced Qs were analyzed by X-ray photoelectron spectroscopy (XPS). Fig. S6 (ESI<sup>†</sup>) shows the XPS full spectra, where no impurities (*e.g.*, Si from silica microspheres) were detected. Fig. 2(b), (c), (e), (f) and (h), (i) present the high-resolution XPS spectra, where both bulk and Qs were shown for comparison. For bulk  $\text{Bi}_2\text{Se}_3$ , as shown in Fig. 2(b) and (c), the two strong peaks at  $158.2$  and  $163.5 \text{ eV}$  corresponded to Bi  $4f_{7/2}$  and Bi  $4f_{5/2}$ , while the two measured peaks at  $53.6$  and  $54.4 \text{ eV}$  were attributed to Se  $3d_{5/2}$  and Se  $3d_{3/2}$ .<sup>32</sup> For  $\text{Bi}_2\text{Se}_3$  Qs, the Bi  $4f$  peaks ( $159.7 \text{ eV}$  for Bi  $4f_{7/2}$  and  $165.0 \text{ eV}$  for Bi  $4f_{5/2}$ ) and Se  $3d$  peaks ( $55.2 \text{ eV}$  for Se  $3d_{5/2}$  and  $56.3 \text{ eV}$  for Se  $3d_{3/2}$ ) all shifted towards higher binding energy by  $1.5$ – $1.9 \text{ eV}$ . As reported previously,<sup>10</sup> the extreme exposure of edge lattices/atoms in  $\text{MoS}_2$  Qs would result in the XPS peak shifting towards lower binding energy. Therefore, the as-observed opposite shifting of the XPS peaks could be driven by the possible change of the topological structure/state in  $\text{Bi}_2\text{Se}_3$  Qs. Similar trends were found in  $\text{Sb}_2\text{Te}_3$  Qs and  $\text{TiS}_2$  Qs. For bulk  $\text{Sb}_2\text{Te}_3$ , as shown in Fig. 2(e) and (f), the peaks at  $528.6$  and  $538.0 \text{ eV}$  were assigned

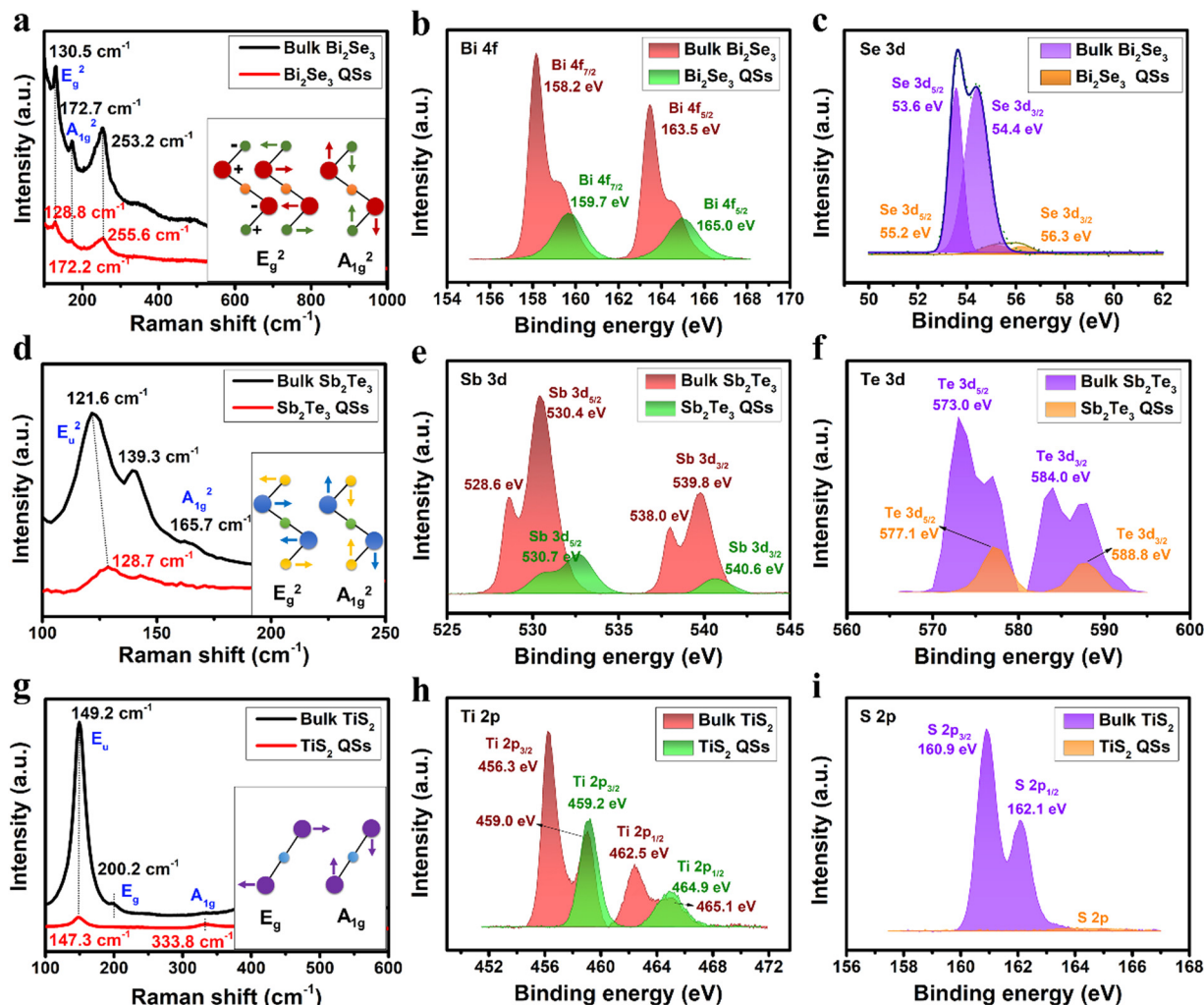


Fig. 2 Spectroscopic characterization of the as-produced QDs. Raman spectra of (a) Bi<sub>2</sub>Se<sub>3</sub> QDs, (d) Sb<sub>2</sub>Te<sub>3</sub> QDs, and (g) TiS<sub>2</sub> QDs. High-resolution XPS spectra of (b), (c) Bi<sub>2</sub>Se<sub>3</sub> QDs, (e), (f) Sb<sub>2</sub>Te<sub>3</sub> QDs, and (h), (i) TiS<sub>2</sub> QDs. Data for bulk materials are shown for comparison.

to Sb 3d<sub>5/2</sub> and Sb 3d<sub>3/2</sub>, while the peaks at 573.0 and 584.0 eV were attributed to Te 3d<sub>5/2</sub> and Te 3d<sub>3/2</sub>. The probable oxidation of bulk Sb<sub>2</sub>Te<sub>3</sub> led to the occurrence of the peaks at 530.4 eV for the Sb 3d<sub>5/2</sub> and 539.8 eV for the Sb 3d<sub>3/2</sub>.<sup>33</sup> For Sb<sub>2</sub>Te<sub>3</sub> QDs, the Sb 3d peaks (530.7 eV for Sb 3d<sub>5/2</sub> and 540.6 eV for Sb 3d<sub>3/2</sub>) and Te 3d peaks (577.1 eV for Te 3d<sub>5/2</sub> and 588.8 eV for Te 3d<sub>3/2</sub>) shifted towards higher binding energy by 2.1–2.6 eV and 4.1–4.8 eV, respectively. For bulk TiS<sub>2</sub>, as shown in Fig. 2(h) and (i), the peaks of Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> were located at 456.3 and 462.5 eV. The two strong peaks at 160.9 and 162.1 eV corresponded to S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub>, consistent with those of 1T-TiS<sub>2</sub>.<sup>23</sup> For TiS<sub>2</sub> QDs, the Ti 2p peaks (459.2 eV for Ti 2p<sub>3/2</sub> and 464.9 eV for Ti 2p<sub>1/2</sub>) shifted towards higher binding energy by 2.9 and 2.4 eV, respectively. The S 2p peaks shifted towards higher binding energy as well, although great suppression of the XPS signal was observed.

The optical properties of the as-produced QDs were investigated, as shown in Fig. 3 and Fig. S7–S11 (ESI<sup>†</sup>). Fig. 3(a)–(c) present the excitation wavelength-, concentration-, and solvent-dependent PL behavior of the Bi<sub>2</sub>Se<sub>3</sub> QD dispersions. A similar

phenomenon could be found in the Sb<sub>2</sub>Te<sub>3</sub> and TiS<sub>2</sub> QD dispersions (Fig. S8–S10, ESI<sup>†</sup>). From Fig. 3(a), the PL intensity reached the maximum at the excitation wavelength of 360 nm for the Bi<sub>2</sub>Se<sub>3</sub> QD dispersions. Such excitation wavelength-dependent PL behavior could be attributed to the size/thickness heterogeneity of the 2D QDs.<sup>8</sup> Fig. 3(b) shows the concentration-dependent PL behavior of the Bi<sub>2</sub>Se<sub>3</sub> QD dispersions. The PL intensity was progressively enhanced with the concentration from 0.001 to 0.025 mg mL<sup>-1</sup> because of the increase of the PL emitters. However, the PL intensity started to decrease with the concentration from 0.025 to 1 mg mL<sup>-1</sup>, which could be ascribed to the aggregation-caused quenching (ACQ) mechanism.<sup>8,34–36</sup> Fig. 3(c) presents the solvent-dependent PL behavior of the Bi<sub>2</sub>Se<sub>3</sub> QD dispersions. The PL intensity of the QD dispersions in varying solvents showed remarkable difference, which could be determined by QD-solvent (direct) interactions.<sup>8,37,38</sup> The PL lifetimes and quantum yields of the QDs were measured, as shown in Fig. 3(d) and Fig. S11 (ESI<sup>†</sup>). The PL lifetimes of Bi<sub>2</sub>Se<sub>3</sub>, Sb<sub>2</sub>Te<sub>3</sub>, and TiS<sub>2</sub> QDs were measured to be approximately 6.6, 7.0, and 3.1 ns, respectively. The

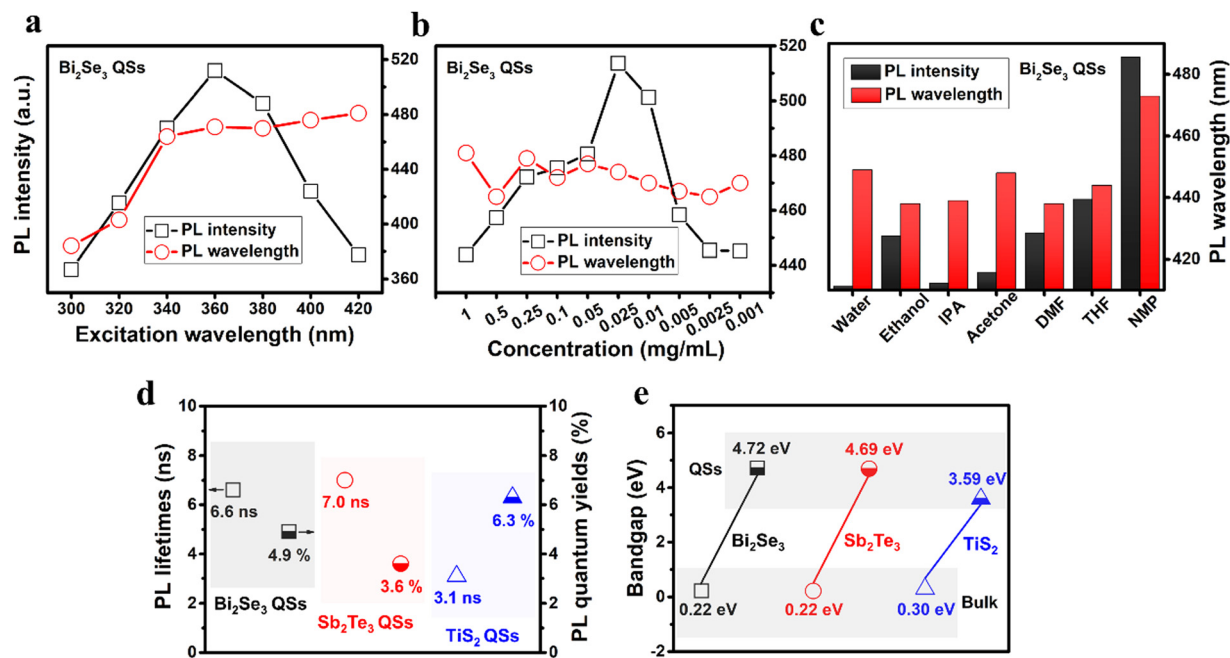


Fig. 3 Photoluminescence of the QS dispersions. (a) Excitation wavelength-dependent PL behavior. (b) Concentration-dependent PL behavior. (c) Solvent-dependent PL behavior. (d) PL lifetimes and quantum yields. (e) Optical bandgap-modulation by size-reduction.

absolute quantum yields were measured to be 4.9, 3.6, and 6.3% for the  $\text{Bi}_2\text{Se}_3$ ,  $\text{Sb}_2\text{Te}_3$ , and  $\text{TiS}_2$  QDs at the wavelength of 360, 360 and 380 nm, respectively. It should be noted that all the examined QDs exhibited blue PL, which could be determined by their bandgaps. The optical bandgaps were derived from the UV-vis absorption spectra, as shown in Fig. S7 (ESI<sup>†</sup>). Fig. 3(e) compares the optical bandgaps between bulk and QDs. For  $\text{Bi}_2\text{Se}_3$ ,  $\text{Sb}_2\text{Te}_3$ , and  $\text{TiS}_2$ , with the sizes down to 2.7, 3.2, and 1.9 nm, the bandgaps increased to 4.72, 4.69, and 3.59 eV, much larger than those (e.g., 0.22, 0.22, 0.30 eV) of bulk materials.<sup>39–41</sup> The as-produced QDs with extremely reduced thickness and lateral size would cause strong (out-of-plane and in-plane) quantum confinement effects, resulting in significant broadening of the optical bandgaps.<sup>42,43</sup> The bandgaps matched well with the blue emission of the QDs. Such (significant) bandgap-widening by (extreme) size-reduction would facilitate the practical applications of the topological insulators and semimetals.

Not only linear but also nonlinear optical performances of the as-produced QDs were explored. Fig. 4(a) shows the schematic setup for the NSA measurements. The laser pulse with wavelengths of 532 and 800 nm, duration of 100 fs, and repetition rate of 1 kHz was incident on an aperture of diameter 4 mm. Fig. S12a (ESI<sup>†</sup>) presents the photographs of the pure PMMA and QDs-PMMA thin films (with the thickness of 120  $\mu\text{m}$  and the edge length of 1 cm). The QDs-PMMA thin films with the fixed loading content of 0.1 wt% demonstrated slightly lower transparency than that of the pure PMMA, further confirmed by UV-vis absorption spectroscopy (Fig. S12b, ESI<sup>†</sup>). Such high transparency would be the basic requirement for future applications. Note that there was no detectable

aggregation/orientation of the QDs in the hybrid thin films, which was determined by the thermodynamic stability of such dispersions.<sup>8</sup> The NSA curves of the QDs-PMMA thin films are shown in Fig. S12c, d and S13 (ESI<sup>†</sup>). The normalized NSA curves (Fig. S13a and b, ESI<sup>†</sup>) were well fitted by the following formula:  $\alpha^*(I) = \alpha_s^*/(1 + I/I_s) + \alpha_{NS}^*$ <sup>44</sup> where  $\alpha^*(I)$  is the absorption coefficient,  $\alpha_s^*$  and  $\alpha_{NS}^*$  are the saturable and non-saturable absorption components,  $I$  is the peak intensity (or power density) of the incident pulsed laser, and  $I_s$  is the saturation intensity defined as the optical intensity required in a steady state to reduce the absorption to half of its unbleached value. Fig. 4(b) summarizes the as-acquired NSA performances of the  $\text{Bi}_2\text{Se}_3$ ,  $\text{Sb}_2\text{Te}_3$ , and  $\text{TiS}_2$  QDs-PMMA thin films. From Fig. 4(b), unprecedented NSA performances were achieved in the QDs-PMMA thin films at wavelengths of both 532 and 800 nm. At 532 nm, the absolute modulation depths of 71.6, 45.1, and 43.6% as well as the saturation intensities of 1.52, 0.82, and 1.53  $\text{MW cm}^{-2}$  (i.e., 152, 82, and 153  $\text{nJ cm}^{-2}$ ) were derived for the  $\text{Bi}_2\text{Se}_3$  QDs-PMMA,  $\text{Sb}_2\text{Te}_3$  QDs-PMMA, and  $\text{TiS}_2$  QDs-PMMA, respectively. At 800 nm, the absolute modulation depths of 72.4, 55.2, and 68.4% as well as the saturation intensities of 0.49, 0.34, and 0.80  $\text{MW cm}^{-2}$  (i.e., 49, 34, and 80  $\text{nJ cm}^{-2}$ ) were achieved for the  $\text{Bi}_2\text{Se}_3$  QDs-PMMA,  $\text{Sb}_2\text{Te}_3$  QDs-PMMA, and  $\text{TiS}_2$  QDs-PMMA, respectively. Note that the  $\text{Bi}_2\text{Se}_3$  QDs-PMMA retained extremely high NSA performances in the visible region, while the  $\text{Sb}_2\text{Te}_3$  QDs-PMMA and  $\text{TiS}_2$  QDs-PMMA demonstrated wavelength-dependent NSA performances. In addition, the  $\text{TiS}_2$  QDs-PMMA showed comparable NSA performances to those of the  $\text{Bi}_2\text{Se}_3$  QDs-PMMA at 800 nm, indicating the great potential in both topological insulators and semimetals. Besides the absolute modulation depths and

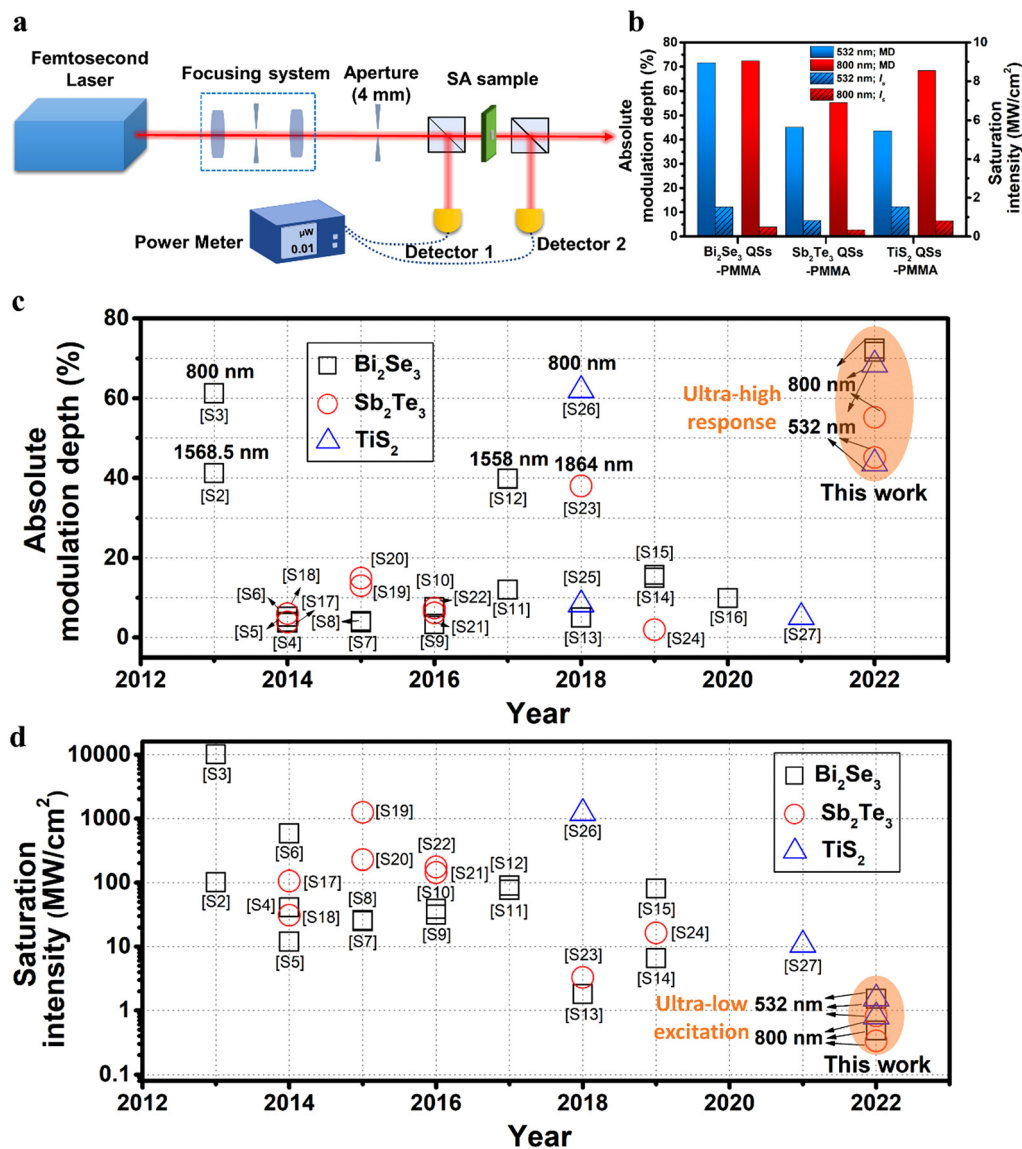


Fig. 4 NLO performances of the QS solid thin films. (a) Schematic setup of the NSA measurement. (b) Plots of the absolute modulation depth and saturation intensity. (c) and (d) NSA performance comparison in topological insulators/semimetals. The references (S2–S27) are listed in Table S1 and the ESI.†

saturation intensities, the relative modulation depths (*i.e.*,  $\alpha_S^*$ ) and nonsaturable losses (*i.e.*,  $\alpha_{NS}^*$ ) were derived, as shown in Fig. S13 (ESI†). All the examined QDs presented high  $\alpha_S^*$  and satisfactory  $\alpha_{NS}^*$ . Particularly, the Bi<sub>2</sub>Se<sub>3</sub> QDs-PMMA demonstrated ultrahigh  $\alpha_S^*$  of 95.9% and extremely low  $\alpha_{NS}^*$  of 4.1%, further supporting its extraordinary NSA performances. Table S1 (ESI†) lists the NSA performances of the as-produced QDs and the topological insulators/semimetals from other works. Based on Table S1 (ESI†), the complete comparison of their NSA performances (*i.e.*, the absolute modulation depths and saturation intensities) was accomplished, as shown in Fig. 4(c) and (d). Excitingly, ultrahigh nonlinear response and ultralow power excitation were simultaneously achieved in the as-produced QDs. Meanwhile, the Bi<sub>2</sub>Se<sub>3</sub> QDs-PMMA demonstrated record-high absolute modulation depth (72.4% at 800 nm),

which had never been achieved before (not limited to topological insulators/semimetals). Such extraordinary NSA performances of the as-fabricated QDs-PMMA thin films could originate from three aspects: (1) the inherent characteristics of the material; (2) intrinsic edge effects; and (3) quantum confinement effect. Firstly, topological insulator/semimetal were a novel state of quantum matter with an insulating bulk state and gapless surface/edge states.<sup>45,46</sup> The unique electronic structure at the surface/edge states of the topological insulator/semimetal made it different from the traditional saturable absorbers (such as graphene, hexagonal boron nitride, transition metal dichalcogenides, In<sub>2</sub>X<sub>3</sub> (X = S, Se, Te), MXene) thus exhibited higher NSA performances.<sup>8,9,47,48</sup> Therefore, the inherent characteristics of topological insulator/semimetal played an important role in the NSA performances. Secondly,

the as-produced Qs possessed entirely exposed edges, maximizing their intrinsic edge effects (nonequilibrium situation (*e.g.*, broken lattices, unsaturated/dangling bonds, dynamic changes, *etc.*) and asymmetric environment). The lattice at the surfaces/edges would dominate compared with their internal lattice in the as-produced Qs. The key roles of the rich surface/edge electronic states on the NSA performances included two aspects: (1) the unique density of states led to a strong overlap between the electronic wavefunctions and incident photons, resulting in an enhanced light-matter interaction. Such interaction facilitated the absorption of the incident light; and (2) the surface/edge electronic states of the as-produced Qs were topologically protected, indicating that they were robust against disorders and perturbations. The robustness of the surface/edge states ensured their effective nonlinear saturation absorption. Hence, the surface/edge (free, nonequilibrium) electronic states played a significant role in their absorption of photons.<sup>49</sup> Thirdly, the extreme size-reduction in the Qs would induce (both in-plane and out-of-plane) quantum confinement effects. Such effects would change the electronic structure, exciton properties and density of states of the as-produced Qs, directly affecting the changes of its nonlinear absorption coefficient, saturation intensity and excited state dynamics, resulting in ultrahigh saturable absorption.<sup>50–52</sup> Evidently, the combination of the inherent characteristics of the material, quantum confinement and intrinsic edge effects could be determinative to their phenomenal NSA performances of the quantum-sized topological insulators and semimetals.

### 3. Conclusions

In summary, quantum-sized topological insulators/semimetals (*i.e.*, Bi<sub>2</sub>Se<sub>3</sub> Qs, Sb<sub>2</sub>Te<sub>3</sub> Qs, and TiS<sub>2</sub> Qs) were produced *via* an all-physical top-down method. The as-produced Qs were monolayers with intrinsic characteristics, which could be determinative to their extraordinary performances. The highly stable QS dispersions presented excitation wavelength-, concentration-, and solvent-dependent PL. The highly transparent Qs-PMMA thin films demonstrated broadband NSA in the visible. Ultrahigh nonlinear response (72.4 and 68.4%) and ultralow power excitation (0.49 and 0.80 MW cm<sup>-2</sup>) were simultaneously achieved in both Bi<sub>2</sub>Se<sub>3</sub> Qs-PMMA and TiS<sub>2</sub> Qs-PMMA. Compared with TiS<sub>2</sub> Qs-PMMA, Bi<sub>2</sub>Se<sub>3</sub> Qs-PMMA maintained extremely high NSA performance at varying (laser) wavelength (532 and 800 nm). Such a highly desired broadband feature in quantum-sized topological insulators would undoubtedly facilitate their applications in mode-locked lasers and related fields.

### Author contributions

Z. C. performed the experiments and characterization studies. Y. Z. supervised the research project. Y. Z. and Z. C. analyzed the data and wrote the manuscript. Z. L. and Y. L. helped with the spectroscopic characterization. X. S. and X. L. performed the nonlinear optical characterization.

### Conflicts of interest

The authors declare no conflict of interest.

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