Research article

Danyun Xu, Zhe Guo, Yudi Tu, Xinzhe Li, Yu Chen, Zhesheng Chen, Bingbing Tian*, Shuqing Chen*, Yumeng Shi, Ying Li, Chenliang Su and Dianyuan Fan

Controllable nonlinear optical properties of different-sized iron phosphorus trichalcogenide (FePS₃) nanosheets

<https://doi.org/10.1515/nanoph-2020-0336>

Received June 18, 2020; accepted August 15, 2020; published online September 2, 2020

Abstract: Two-dimensional iron phosphorus trichalcogenide (FePS₃) has attracted significant attention for its use in electricity, magnetism and optical fields due to its outstanding physical and chemical properties. Herein, FePS₃ was prepared using the chemical vapor transportation (CVT) method and then exfoliated by using fast electrochemical exfoliation. After gradient centrifugation, FePS₃ nanosheets with thicknesses ranging from 1.5 to 20 nm and lateral dimensions of 0.5–3 μm were obtained. By utilizing the spatial self-phase modulation (SSPM) effect, the relationships between the nonlinear refractive index and the size of the FePS₃ nanosheets were investigated in detail which revealed that the nonlinear refractive index can be effectively controlled by the size of the FePS₃ nanosheets. It is worth noting that the optimal FePS₃ nanosheets (3–5 layers thick and $\sim 1 \mu\text{m}$ in lateral dimensions) displayed the highest nonlinear refractive index of $\sim 10^{-5} \text{ cm}^2 \text{ W}^{-1}$. This work demonstrates the potential that FePS₃ nanosheets have for use in nonlinear optics or nonlinear optical devices.

*Corresponding authors: Bingbing Tian and Shuqing Chen, International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education, Institute of Microscale Optoelectronics, Shenzhen University, Shenzhen 518060, China, E-mail: tianbb2011@szu.edu.cn (B. Tian), shuqingchen@szu.edu.cn (S. Chen). <https://doi.org/10.0000-0002-2321-4760> (S. Chen). <https://orcid.org/10.0000-0003-1508-6217> (B. Tian)

Danyun Xu, Zhe Guo, Yudi Tu, Xinzhe Li, Yu Chen, Yumeng Shi, Ying Li, Chenliang Su and Dianyuan Fan, International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education, Institute of Microscale Optoelectronics, Shenzhen University, Shenzhen 518060, China **Zhesheng Chen,** International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education, Institute of Microscale Optoelectronics, Shenzhen University, Shenzhen 518060, China; and Laboratoire de Physique des Solides, CNRS, Université Paris Saclay, Orsay 91405, France

Keywords: electrochemical exfoliation; FePS₃ nanosheets; gradient centrifugation; nonlinear optical properties; spatial self-phase modulation.

1 Introduction

Metal phosphorus trichalcogenides (MPTs) have drawn considerable interest in recent years due to their excellent magnetic, electronic, and optical properties for applications in catalysis, energy storage, and optoelectronic devices [1–8]. MPTs have a general structure of MPX_3 , where M stands for a transition metal (Fe, Co, Ni, Cr, Mn, etc.) and X is S or Se. A monolayer sheet in the MPX_3 structure consists of covalent- and ionic-bonded metal (M^{2+}) and phosphorus atoms sandwiched between two layers of X atoms, forming a stable bipyramid structure of $(\text{P}_2\text{X}_6)^{4-}$, similar to the superlattices of transition metal dichalcogenides (TMDs). The interlayers are held together by van der Waals forces with lower cleavage energies (0.29–0.54 J m^{-2}) [9] relative to graphite (0.37 J m^{-2}) [10], suggesting that MTP flakes can be exfoliated from their corresponding bulk crystals [11, 12]. Because of their ionic bonding, MTPs flakes show different physical and chemical properties and weaker interlayer cleavage energies relative to graphene and TMDs [13–15]. In addition, MPTs are a family of semiconductors with a tunable bandgap ranging from 1.3 to 3.5 eV that can be modified by changing the metal atoms and the number of layers [16]. Because of these properties, MPTs have shown higher absorption efficiency and broader absorption range compared to other two-dimensional (2D) materials [17], which is the cause of their excellent nonlinear optical properties.

For example, the nonlinear optical properties of NiPS₃ nanosheets have been investigated by Z-scan measurements to generate picosecond laser pulses with a 1- μm band in the fast cavity [18]. Iron phosphorus trichalcogenide (FePS₃) possesses a bandgap ranging from 1.60 (bulk) to 2.18 eV (monolayer) and shows substantially accelerated

photocatalytic H₂ production rates [6]. Moreover, FePS₃ nanosheets have also been reported to have coexisting positive and negative photoconductivity for applications as ultraviolet photodetectors [19]. By taking advantage of these features, FePS₃ nanosheets could have potential applications in the nonlinear optics field. Recently, the nonlinear refractive indexes for a series of 2D materials have been accurately acquired based on spatial self-phase modulation (SSPM), such as TMDs [20], black phosphorus [21] and graphdiyne [22]. However, there are few studies on the nonlinear optical properties of FePS₃ nanosheets, especially studies on the size-dependent structural optical properties of FePS₃ nanosheets and their application in field of optical devices.

Herein, we demonstrate the production of high-quality FePS₃ nanosheets obtained by the rapid electrochemical exfoliation of chemical vapor transportation (CVT)-grown FePS₃ crystals. With the aid of gradient centrifugation, FePS₃ nanosheets with different sizes have been obtained with thicknesses ranging from 1.5 to 20 nm and lateral dimensions of 0.5–3 μm. The third-order nonlinear optical properties of these nanosheets were also explored using SSPM. The size of the FePS₃ nanosheets was found to effectively control the nonlinear refractive indexes of FePS₃.

2 Experimental section

2.1 Chemicals

All the starting chemicals were purchased commercially and used without further purification. Specifically, tetra-*n*-butylammonium tetrafluoroborate (TBAB, C₁₆H₃₆BF₄N, 99%), iron powder (Fe, 99.99%) and red phosphorus powder (P, 99.99%) were purchased from Alfa Aesar (Beijing, China). Sulfur powder (S, 99.999%) was purchased from Aladdin (Shanghai, China). Propylene carbonate (PC, 99%), *N,N*-dimethylformamide (DMF, 99.5%), isopropyl alcohol (IPA, 99.5%) and polyvinyl pyrrolidone (PVP, 99%, molecular weight of 50,000) were purchased from Macklin (Shenzhen, China).

2.2 Preparation of bulk FePS₃ crystals

The CVT method was used to prepare the bulk FePS₃ crystals. Two grams of phosphorus, iron, and sulfur powders mixed in a stoichiometric molar ratio (1:1:3) were ground in an inert atmosphere glovebox. The mixed powders were sealed in a vacuum quartz tubes (length of 25 cm, internal diameter of 11 mm and wall thickness of 1 mm) under a pressure of 10^{−5} Pa via a Partulab device (MRVS-1002, China) equipped with a hydrogen/oxygen welding

torch to obtain hermetically sealed tubes full of powder. The sealed tubes were placed in a two-zone furnace at a reaction temperature of 750 °C and growth temperature of 700 °C at a heating rate of 1 °C min^{−1} for nine days to create a temperature gradient for growing the bulk crystals. Finally, the bulk FePS₃ crystals were successfully obtained after the furnace was cooled to room temperature.

2.3 Preparation of exfoliated FePS₃ nanosheets

Compared with other exfoliation methods such as chemical vapor deposition, mechanical exfoliation and liquid-phase exfoliation, electrochemical exfoliation exhibits some merits of large-scale fabrication, high-quality, environmental-protection, time-saving and controllable-layer [23–26]. Here, exfoliated FePS₃ nanosheets were obtained by applying a direct current (DC) bias (−2.5 V) to the bulk FePS₃ crystals with an electrochemical workstation (CHI 760E, Beijing Huake Putian, China) in a two-electrode system. Bulk FePS₃ crystals were used as the working electrode by fixing the bulk crystals on a platinum electrode holder and a platinum wire was employed as the counter electrode. The electrolyte consisted of 60 mg of TBAB dissolved in 30 mL of PC. Similar to the previous work [26], TBAB salts were firstly driven to intercalate into the interlayer of bulk FePS₃ crystals using a constant bias for seconds. And then lasting for a long time, some gaseous species were generated due to the electrochemical decomposition of TBAB salts, benefiting to the ultrafast volume exfoliation of FePS₃ crystals. Finally, a suspension was harvested by manual-shaking for approximately 20 s. The suspension was then centrifuged to collect the expanded FePS₃ which was then redispersed into DMF with 10 mg mL^{−1} PVP by using an ultrasonic water bath for 30 min. The dispersed suspension was then centrifuged to remove the unexfoliated FePS₃, and the supernatant was washed with a large quantity of DMF and IPA by centrifugation. Finally, the FePS₃ nanosheets were redispersed into IPA for further characterization and utilization. Additionally, we applied gradient centrifugation to obtain FePS₃ nanosheets of different sizes, which is beneficial for identifying any size-related effects and the inherent nonlinear optical properties of FePS₃.

2.4 SSPM of FePS₃ nanosheets

This SSPM effect has been widely used to explore the nonlinear optical properties of low-dimensional materials [27]. In this experiment, 532 nm (MGL-S-300 mW, Shenzhen, China) and 633 nm (HNL210LB, Shenzhen, China) lasers

were used as the light sources to investigate the SSPM response of FePS₃ nanosheets dispersed in IPA in a 1-mm-thick cuvette. The light profile by the power meter (1919-R, Shenzhen, China) was recorded with a charge-coupled device (CCD) device (WinCamD-UCD 15, Shenzhen, China). All the samples were investigated at the same concentration of 0.28 mg/L. The formulas used to obtain the corresponding nonlinear optical coefficients are as follows.

From the basis of the nonlinear optical Kerr effect, the refractive indexes were determined by $n = n_0 + n_2 I$, where n_0 is the linear refractive index, the nonlinear refractive index is n_2 and I symbolizes the incident intensity. IPA was employed as the dispersing solvent, so the value of n_0 is 1.42 [28]. n_2 is defined by the following formula [29]:

$$n_2 = \frac{\lambda}{2n_0 L_{\text{eff}}} \cdot \frac{N}{I} \quad (1)$$

where λ , L_{eff} , and N stand for the incident laser wavelength, the effective optical length of the sample solution dispersion, and the ring numbers, respectively. L_{eff} can be calculated by [28]:

$$L_{\text{eff}} = \int_{L_2}^{L_1} \left(1 + \frac{z^2}{z_0^2} \right)^{-1} dz = z_0 \arctan \left(\frac{z}{z_0} \right) \Big|_{L_2}^{L_1} \quad (2)$$

where L_1 and L_2 are the distance between the focal point and the two sides of cuvette and the thickness of the cuvette is defined as L ($L = L_1 - L_2$). $z_0 = \omega_0^2 / \lambda$ (z_0 is the diffraction length, while z is 0 and ω_0 stands for the $1/e^2$ beam radius of the 0.03 cm incident laser). The corresponding third-order nonlinear susceptibility ($\chi_{\text{total}}^{(3)}$) can be obtained from the following equation [28]:

$$\chi_{\text{total}}^{(3)} = \frac{c \lambda n_0}{2.4 \times 10^4 \pi^2 L_{\text{eff}}} \cdot \frac{dN}{dI} \quad (3)$$

2.5 Characterization

The size distribution of the FePS₃ nanosheets was analyzed in IPA by using a laser particle size analyzer (DelsaMax CORE, Beckman Coulter, USA). The morphology of the FePS₃ nanosheets was determined by using atomic force microscopy (AFM, Dimension ICON system, Bruker, USA). A scanning electron microscope (SEM, TESCAN-MIRA3, Shanghai, China) was employed to characterize the cross section of the FePS₃ crystals before and after intercalation. The morphology of the FePS₃ nanosheets collected at different centrifugation speeds was observed using a high-resolution transmission electron microscope (HR-TEM, FEI Tecnai G20/JEM2010, FEI Company, USA). Raman spectra were recorded using a WITec (Alpha300 system, USA) with

an excitation laser wavelength of $\lambda = 532$ nm. The absorbance spectrum of the FePS₃ nanosheets dispersed in IPA was recorded from 200 to 1000 nm with a UV-vis spectrophotometer (Agilent Cary5000, USA). The X-ray diffraction (XRD) spectra of FePS₃ materials were characterized by XRD (Ultima IV, Japan). All of the characterization measurements were performed at room temperature.

3 Results and discussion

Bulk FePS₃ single crystals were synthesized by CVT method (Figure 1a, see Supplementary material for details). Their XRD spectra show an intense c -axis orientation and the obtained peaks coincided well with the pattern of the FePS₃ standard XRD data (JCPDS no. 30-0663) [30], suggesting the phase purity and high crystallinity of synthesized FePS₃ single crystals (Figure S2). High quality FePS₃ nanosheets were then obtained by electrochemical exfoliation of the bulk FePS₃ single crystals using a two-electrode system with TBAB as the electrolyte (Figure 1b) [26, 31, 32]. After manual shaking, sonicating, removing the unexfoliated FePS₃ and washing, the FePS₃ nanosheets were finally dispersed in an IPA solution for the following application, which show an obvious Tyndall effect (Figure 1c). As shown in XRD spectra of exfoliated nanosheets (Figure S3), a strong peak is placed at 13.8° indexing to (0 0 1) and three small peaks of (0 0 2), (0 0 3) and (0 0 4) patterns are, respectively, located at 27.8°, 42.4° and 57.6°. Although the intensities of these peaks are weaker than that of the bulk counterpart, their position has no shifts, meaning that the crystallinity of nanosheets has been maintained. These results indicate the successful achievement of the exfoliation from the bulk crystals into thin nanosheets. The exfoliation mechanism is illustrated in Figure 1d, and the size-separation procedure for the FePS₃ nanosheets using gradient centrifugation is shown in Figure S6. After screening by gradient centrifugation (Figure S6), FePS₃ nanosheets of different sizes were obtained. These different sized FePS₃ nanosheets suspensions were quite stable when stored under ambient conditions for more than 30 days (Figure S7). The size of the FePS₃ nanosheets in the suspensions decreased as the rotation speed increased.

The sizes of the FePS₃ nanosheets dispersed in IPA after centrifugation at different speeds are shown in the inset of Figure 2a. The FePS₃ nanosheet suspensions are homogeneous and yellowish-brown and became darker with decreasing centrifugal speeds due to the increased size of the nanosheets. The absorbance of the suspensions decreased with increasing centrifugal speed and shows no prominent absorption peaks (Figure 2a), similar to

Figure 1: The electrochemical cathodic exfoliation process.

(a) Pictures of bulk iron phosphorus trichalcogenide (FePS₃) single crystals. (b) Diagrams of the equipment used for electrochemical exfoliation. (c) From left to right: pictures of the expanded FePS₃, a dispersed FePS₃ solution after manual shaking, a dispersed FePS₃ solution after sonication and the final FePS₃ dispersion produced via centrifugation showing the Tyndall effect. (d) Illustration of the mechanism of electrochemical exfoliation process for bulk FePS₃ crystals using tetra-*n*-butylammonium as the electrolyte salt.

previous reports [19]. Furthermore, AFM measurements were used to precisely analyze the size distribution of the FePS₃ nanosheets. Typical AFM images of the FePS₃ nanosheets acquired at different centrifugal speeds are shown in Figure 2b–g. FePS₃ nanosheets of different sizes are all 2D in structure, verifying the successful exfoliation of the bulk FePS₃ crystals. Some aggregated particles are also present in the AFM images, probably due to reaggregation occurring during the repeated dispersion and centrifugation steps. Comprehensive statistics of all nanosheets obtained at centrifugation speeds over or under 1000 rpm show that the FePS₃ nanosheets have an average thickness of ~5.5 nm and an average lateral dimension of ~1 μm (Figures S8–S11a), the corresponding number of layers can be estimated as 3–4 layers [33]. As the centrifugation speed decreases, most of the collected nanosheets have lateral dimensions of 0.5–3 μm and a thickness of 1.5–20 nm (1–15 layers). However, some nanosheets with thicknesses of 5 nm were present under centrifugation speeds of 7000 rpm or less, most likely due to the large lateral dimension of these nanosheets. Therefore, the size distribution obtained by gradient centrifugation should consider both the lateral dimensions and the thickness of the nanosheets. The average size (lateral dimension and thickness) decreased as the centrifugation speed increased. The size distributions of the FePS₃ nanosheets at different centrifugation speeds obtained

from the AFM images matches well with the hydrodynamic size distributions measured by the particle-size description analyzer (Figure S11). Moreover, the results shown in the AFM images are also consistent with the TEM results (Figure S12). High-resolution TEM images and the corresponding elemental mapping analysis obtained for the nanosheets collected at a centrifugation speed of 5000 rpm are shown in Figure S12f, which demonstrates the uniform distribution of the Fe, P and S elements.

Raman spectroscopy is a powerful and widely used technique for characterizing the structure of van der Waals-stacked materials and for revealing differences between bulk materials and the corresponding exfoliated nanosheets. The bulk FePS₃ has a monoclinic structure with C₂ symmetry which displays five Raman active modes attributed to vibrations of the iron cations (C Raman active modes) and (P₂S₆)⁴⁻ bipyramid structures with D_{3d} symmetry (A_{1g}⁽¹⁾, A_{1g}⁽²⁾ and E_g⁽¹⁾, E_g⁽²⁾ Raman active modes), as shown in Figure 2h. Near 157 cm⁻¹, there is a highly Raman active counterpart of an infrared active Eu-type mode vibration originating from the (P₂S₆)⁴⁻ unit. The A_{1g}⁽¹⁾ and A_{1g}⁽²⁾ vibrations are at approximately 380 and 248 cm⁻¹, respectively, which are caused by the out-of-plane phonon modes, while the two in-plane vibrations (E_g⁽¹⁾ and E_g⁽²⁾) are at approximately 279 and 227 cm⁻¹, respectively. These results are consistent with previous studies on the Raman vibration modes of the FePS₃ [34]. After exfoliation,

Figure 2: (a) UV-vis absorbance spectra of iron phosphorus trichalcogenide (FePS₃) nanosheet dispersions from different centrifugation speeds with the corresponding pictures in the inset. Atomic force microscopy (AFM) images of FePS₃ nanosheets with corresponding thickness and lateral size distributions from different centrifugation speeds of (b) 1000, (c) 3000, (d) 5000, (e) 7000 and (f) 9000 rpm with (g) the thickness step scale bar of -20 to 25 μm. (h) Raman spectra of bulk FePS₃ crystals (black) and FePS₃ nanosheets obtained from different centrifugation speeds of 1000 rpm (magenta), 3000 rpm (orange), 5000 rpm (green), 7000 rpm (cyan) and 9000 rpm (blue). It should be noted that all samples with different Raman intensities were characterized under the same conditions on a SiO₂/Si substrate at a laser excitation wavelength of 532 nm. The spectral features at approximately 527 and 300 cm⁻¹ represent the first-order and second-order Raman peak of silicon, respectively.

Figure 2h shows there is an absence of the Eu-type mode, suggesting the presence of only few- and single-layer FePS₃ nanosheets [6]. The sharp features of the A_g⁽¹⁾ and the other

Raman vibration modes in the Raman spectra indicate that the FePS₃ nanosheets have retained a stable structure [30]. Furthermore, an obvious distinction between the bulk and

exfoliated materials is the Raman shift of the iron cation vibration (C), which is also indicative of the success of the exfoliation process [16, 35]. Notably, compared to the MoS₂, the interlayer Raman active modes display weakened Raman signal with decreased centrifugation speed, implying there are weaker interlayer van der Waals forces than those found in most other van der Waals-stacked materials [16].

To study the nonlinear optical behavior of the FePS₃ nanosheets, typical measurements based on the SSPM effect were performed with 532 and 633 nm laser excitation sources as shown in Figure 3a. The laser beam traversed the FePS₃ nanosheet dispersions and interacted with the FePS₃ nanosheets. Once the power of the 532 nm incident light beam exceeded the excitation threshold of the nonlinear effect, a series of representative diffraction rings appeared from the center of the pattern with gradually increasing diameters (Figure S14) because of the non-uniform light intensity distribution on the beam cross-section, which is typical of the SSPM effect. To thoroughly investigate the influence that the size of the FePS₃ nanosheets has on the nonlinear optical properties, different centrifugation speeds were used to obtain FePS₃ nanosheets of different sizes. The corresponding relationship between the number of rings and incident intensity at different centrifugal speeds is shown in Figure 3b for systematic comparison. It can be seen in Figure 3b that the number of rings increases linearly in proportion to the incident intensity. Under different centrifugation speeds, the slopes (dN/dI) can be significantly different, which means that the nonlinear refractive index coefficient can be regulated and controlled. Most importantly, the FePS₃ nanosheets centrifuged at 5000 rpm possess the highest slope (dN/dI) and the smallest threshold for the SSPM effect. These results are consistent with previous reports on gap-dependent SSPM [20], and can help further explain how the size of the SSPM diffraction rings are dependent on the intensity of the laser due to the intrinsic bandgap varying with changes in the size of the nanosheets. Notably, the FePS₃ nanosheets obtained at 5000–3000 rpm display higher slopes, which makes sense because the FePS₃ nanosheets from this centrifugation speed are approximately ~7 nm in thickness and have lateral dimensions of ~1 μ m and show better nonlinear optical absorption. To further understand the value of highest slopes, the curve for the ring number versus the incident intensity at 5000 rpm is shown in Figure 3c. The highest slopes (dN/dI) are 0.4731 at the wavelength $\lambda = 532$ nm, while at 633 nm, the slope is 0.1219. Combining the linear fitting slopes and formulas (1), (2) and (3) introduced in the methods, the corresponding nonlinear optical coefficients were calculated, namely, the corresponding nonlinear refractive coefficients (n_2), which are $8.86 \times 10^{-5} \text{ cm}^2 \text{ W}^{-1}$ (532 nm) and $2.72 \times 10^{-5} \text{ cm}^2 \text{ W}^{-1}$

(633 nm), respectively. The corresponding third-order nonlinear susceptibilities $\chi_{\text{total}}^{(3)}$ for the FePS₃ nanosheets are 4.56×10^{-5} (e.s.u.) (532 nm) and 1.40×10^{-5} (e.s.u.) (633 nm). Considering that $E_{\text{total}} = \sum_{i=1}^M E_i \approx M E_{\text{single layer}}$, where M stands for the effective layer number of the FePS₃ nanosheets, then $\chi_{\text{single layer}}^{(3)}$ can be calculated using $\chi_{\text{total}}^{(3)} = M^2 \chi_{\text{single layer}}^{(3)}$. In this experiment, M is in the order of ~100 (Figure S5), so $\chi_{\text{single layer}}^{(3)}$ is estimated to be ~ 10^{-9} at wavelengths of 532 and 633 nm. Other typical 2D materials have been listed in Table S1, showing the variation of optical parameters with wavelength of laser lights.

After prolonging the irradiation time, there was an expected phenomenon where the diffraction rings began to rapidly distort as shown in Figure 3d. At 1.1 s, a semi-circular diffraction ring formed as the upper half of the diffraction rings collapsed toward the center. This phenomenon can be explained by thermal effects [29]. To further investigate the impact of this distortion on the measured nonlinear refractive index of the FePS₃ nanosheets, the angles that formed between the sample and the pattern were used to analyze the variations of the collapse distortion in Figure 3d. When a laser travelled through the sample, a complete diffraction ring appeared on the screen with the corresponding maximum diffractive radius of R_H and a distortion angle of θ_H . Following the distortion event, the upper half of the diffraction ring was changed and the new maximum diffractive radius and new distortion angle are named R'_H and θ'_D respectively. The corresponding distorted diffraction radius and angle are marked with R_D and θ_D . By learning from the previous equation [28, 36] (Equations (1)–(8) in Supplementary material) and parameters, the relation ($\Delta n_2/n_2 = \theta_D/\theta_H$) is used to explain the relative variations of the nonlinear refractive index with the collapse angle under the condition of D (the distance between the sample and screen) $\gg R_H$ or R'_H . As shown in Figure 3e, the half-cone angle (θ_H) and distortion angle (θ_D) change linearly with the incident intensity. However, the ratio of θ_D/θ_H increases first and then tends toward saturation with increasing incident intensity, as shown in Figure 3f. Considering that θ_D/θ_H equates to $\Delta n_2/n_2$, the light intensity finally results in changes of Δn_2 for the nonlinear refractive index of n_2 . Therefore, under strong light intensity or for extended laser irradiation times, a collapse will occur due to heating effect of the FePS₃ nanosheets, resulting in measurement errors for n_2 .

To explore the interactions between light and the FePS₃ nanosheets, an illumination experiment was performed as shown in Figure 4. The FePS₃ nanosheets obtained at 5000 rpm have a bandgap of ~2.22 eV (Figure 4a),

Figure 3: (a) Spatial self-phase modulation (SSPM) experiments for the iron phosphorus trichalcogenide (FePS₃) nanosheet solutions with experimental images. (b) Diagram of the relationship between the diffraction rings and the corresponding incident intensity for the FePS₃ dispersion obtained from different centrifugation speeds at $\lambda = 532$ nm. (c) Diffraction rings of the FePS₃ dispersion obtained at 5000 rpm as a function of the incident intensity with laser wavelengths of 532 nm (green) and 633 nm (red). (d) Schematic diagram showing the distortion of the FePS₃ nanosheet dispersions. (e) The half-cone angle (θ_H) and the corresponding distortion angle (θ_D) as a function of the incident intensity at a laser wavelength of 532 nm. (f) Variation from the nonlinear refractive index of FePS₃ before and after distortion using ExpDec1 fitting.

Figure 4: (a) (i) UV-vis-NIR diffusive reflectance absorption spectra and (ii) the curve for the transformed Kubelka–Munk function with the photon energy for the FePS₃ nanosheets collected at 5000 rpm. The FePS₃ nanosheets are an indirect semiconductor with a corresponding bandgap of ~ 2.22 eV. (b) The mechanism for the interactions between the light and the FePS₃ nanosheets with the optical-bandgap structure in which the location of the conduction band minimum (CBM) is at the K point and the corresponding valence band maximum (VBM) is along the $K \rightarrow \Gamma$ path, showing the excitation spectrum of the free carriers of FePS₃.

close to the theoretical optical bandgap of monolayer FePS₃ (2.54 eV) [9]. Light sources with wavelengths of 532 and 633 nm can be used to excite electrons during their interaction with the FePS₃ nanosheets. In particular, the wavelength 532 nm is used to excite the electrons of materials with optical bandgaps smaller than 2.33 eV, while 633 nm is appropriate for materials with optical bandgaps below 1.96 eV. The electrons in the valence band are excited after absorbing incident photons and are promoted to the conduction band by overcoming the energy barrier of the interband transition (Figure 4b). The movements of these electrons are connected to oscillations of the electromagnetic field, resulting in the reorientation and alignment of the FePS₃ nanosheets, which is the origin of their nonlinear optical properties [29].

4 Conclusion

In conclusion, different sized FePS₃ nanosheets were successfully obtained by combining electrochemical exfoliation of high-quality FePS₃ crystals with gradient centrifugation. The nonlinear optical response of the FePS₃ nanosheets based on SSPM was further developed to understand the nonlinear optical properties of the FePS₃ nanosheets and any size-dependent effects. The obtained FePS₃ nanosheets show obvious excitation wavelength SSPM, especially the nanosheets that were 3–5 layers thick with lateral dimensions of ~ 1 μ m. The superior nonlinear refractive index reached values of $\sim 10^{-5}$ cm² W⁻¹ and the

corresponding third-order nonlinear susceptibility was in the order of $\sim 10^{-9}$. These experimental results indicate that FePS₃ nanosheets have exceptional promise for applications in all kinds of nonlinear and optoelectronic devices and open the door for the use of other MTPs in the nonlinear optical field based on the SSPM effect.

Acknowledgements: The authors acknowledge the financial support from the Guangdong Natural Science Funds (2019A151010675), the Science and Technology Project of Shenzhen (Grant Nos. JCYJ20180305125106329, JCYJ20180305124927623 and ZDSYS201707271014468), the Shenzhen Peacock Plan (Grant Nos. 827-000273, KQJSCX20180328094001794 and KQTD2016053112042971). Prof. C. Su thanks the support from the Guangdong Special Support Program, and the Pengcheng Scholar Program.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: The authors acknowledge the financial support from the Guangdong Natural Science Funds (2019A151010675), the Science and Technology Project of Shenzhen (Grant Nos. JCYJ20180305125106329, JCYJ20180305124927623 and ZDSYS201707271014468), the Shenzhen Peacock Plan (Grant Nos. 827-000273, KQJSCX20180328094001794 and KQTD2016053112042971).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

- [1] X. Wang, Z. Song, W. Wen, et al., "Potential 2D materials with phase transitions: structure, synthesis, and device applications," *Adv Mater.*, vol. 31, no. 45, pp. 1804682–1804695, 2019.
- [2] X. Zhang, Z. Luo, P. Yu, et al., "Lithiation-induced amorphization of Pd₃P₂S₈ for highly efficient hydrogen evolution," *Nat. Catal.*, vol. 1, no. 6, pp. 460–468, 2018.
- [3] S. Xue, L. Chen, Z. Liu, H. M. Cheng, and W. Ren, "NiPS₃ nanosheet-graphene composites as highly efficient electrocatalysts for oxygen evolution reaction," *ACS Nano*, vol. 12, no. 6, pp. 5297–5305, 2018.
- [4] Q. Liang, Y. Zheng, C. Du, et al., "Asymmetric-layered tin thiophosphate: an emerging 2D ternary anode for high-performance sodium ion full cell," *ACS Nano*, vol. 12, no. 12, pp. 12902–12911, 2018.
- [5] C. F. Du, Q. Liang, R. Dangol, et al., "Layered trichalcogenidophosphate: a new catalyst family for water splitting," *Nanomicro Lett.*, vol. 10, no. 4, pp. 67–81, 2018.
- [6] Z. Cheng, T. A. Shifa, F. Wang, et al., "High-yield production of monolayer FePS₃ quantum sheets via chemical exfoliation for efficient photocatalytic hydrogen evolution," *Adv. Mater.*, vol. 30, no. 26, pp. 1707433–1707438, 2018.
- [7] F. M. Wang, T. A. Shifa, P. Yu, et al., "New Frontiers on van der Waals layered metal phosphorous trichalcogenides," *Adv. Funct. Mater.*, vol. 28, no. 37, pp. 1802151–1802174, 2018.
- [8] T. A. Shifa, F. Wang, Z. Cheng, et al., "High crystal quality 2D manganese phosphorus trichalcogenide nanosheets and their photocatalytic activity," *Adv. Funct. Mater.*, vol. 28, no. 18, pp. 1800548–1800555, 2018.
- [9] X. Zhang, X. Zhao, D. Wu, Y. Jing, and Z. Zhou, "MnPSe₃ monolayer: a promising 2D visible-light photohydrolytic catalyst with high carrier mobility," *Adv. Sci. Wein.*, vol. 3, no. 10, pp. 1600062–1600066, 2016.
- [10] R. Zacharia, H. Ulbricht, and T. Hertel, "Interlayer cohesive energy of graphite from thermal desorption of polyaromatic hydrocarbons," *Phys. Rev. B*, vol. 69, no. 15, pp. 155406–155412, 2004.
- [11] X. Li, X. Wu, and J. Yang, "Half-metallicity in MnPSe₃ exfoliated nanosheet with carrier doping," *J. Am. Chem. Soc.*, vol. 136, no. 31, pp. 11065–11073, 2014.
- [12] D. Mukherjee, P. M. Austeria, and S. Sampath, "Two-dimensional, few-layer phosphochalcogenide, FePS₃: a new catalyst for electrochemical hydrogen evolution over wide pH range," *ACS Energy Lett.*, vol. 1, no. 2, pp. 367–372, 2016.
- [13] M. A. Susner, M. Chyasnachyus, M. A. McGuire, P. Ganesh, and P. Maksymovych, "Metal thio- and selenophosphates as multifunctional van der Waals layered materials," *Adv. Mater.*, vol. 29, no. 38, pp. 1602852–1602890, 2017.
- [14] R. Gusmão, Z. Sofer, D. Sedmidubský, Š. Huber, and M. Pumera, "The role of the metal element in layered metal phosphorus triselenides upon their electrochemical sensing and energy applications," *ACS Catal.*, vol. 7, no. 12, pp. 8159–8170, 2017.
- [15] R. N. Jenjeti, M. P. Austeria, and S. Sampath, "Alternate to molybdenum disulfide: a 2D, few-layer transition-metal thiophosphate and its hydrogen evolution reaction activity over a wide pH range," *ChemElectroChem*, vol. 3, no. 9, pp. 1392–1399, 2016.
- [16] K. Z. Du, X. Z. Wang, Y. Liu, et al., "Weak van der Waals stacking, wide-range band gap, and Raman study on ultrathin layers of metal phosphorus trichalcogenides," *ACS Nano*, vol. 10, no. 2, pp. 1738–1743, 2016.
- [17] J. F. Liu, Y. W. Wang, Y. Y. Fang, et al., "A robust 2D photo-electrochemical detector based on NiPS₃ flakes," *Adv. Electron. Mater.*, vol. 5, no. 12, pp. 1900726–1900733, 2019.
- [18] J. Liu, X. Li, Y. Xu, et al., "NiPS₃ nanoflakes: a nonlinear optical material for ultrafast photonics," *Nanoscale*, vol. 11, no. 30, pp. 14383–14391, 2019.
- [19] Y. Gao, S. Lei, T. Kang, et al., "Bias-switchable negative and positive photoconductivity in 2D FePS₃ ultraviolet photodetectors," *Nanotechnology*, vol. 29, no. 24, pp. 244001–244007, 2018.
- [20] Y. Wu, Q. Wu, F. Sun, C. Cheng, S. Meng, and J. Zhao, "Emergence of electron coherence and two-color all-optical switching in MoS₂ based on spatial self-phase modulation," *Proc. Natl. Acad. Sci. U. S. A.*, vol. 112, no. 38, pp. 11800–11805, 2015.
- [21] J. Zhang, X. Yu, W. Han, et al., "Broadband spatial self-phase modulation of black phosphorous," *Opt. Lett.*, vol. 41, no. 8, pp. 1704–1707, 2016.
- [22] L. Wu, Y. Dong, J. Zhao, et al., "Kerr nonlinearity in 2D graphdiyne for passive photonic diodes," *Adv. Mater.*, vol. 31, no. 14, pp. 1807981–1807990, 2019.
- [23] C. T. Kuo, M. Neumann, K. Balamurugan, et al., "Exfoliation and Raman spectroscopic fingerprint of few-layer NiPS₃ van der Waals crystals," *Sci. Rep.*, vol. 6, p. 20904, 2016.
- [24] J. Chang, G. Wang, A. Belharsa, J. Ge, W. Xing, and Y. Yang, "Stable Fe₂P₂S₆ nanocrystal catalyst for high-efficiency water electrolysis," *Small Methods*, vol. 4, no. 6, p. 1900632, 2019.
- [25] Y. Guo, C. Liu, Q. Yin, et al., "Distinctive in-plane cleavage behaviors of two-dimensional layered materials," *ACS Nano*, vol. 10, no. 9, pp. 8980–8988, 2016.
- [26] X. Li, Y. Fang, J. Wang, et al., "High-yield electrochemical production of large-sized and thinly layered NiPS₃ flakes for overall water splitting," *Small*, vol. 15, no. 30, pp. 1902427–1902436, 2019.
- [27] X. J. Zhang, Z. H. Yuan, R. X. Yang, et al., "A review on spatial self-phase modulation of two-dimensional materials," *J. Cent. South Univ.*, vol. 26, no. 9, pp. 2295–2306, 2019.
- [28] L. M. Wu, Z. J. Xie, L. Lu, et al., "Few-layer tin sulfide: a promising black-phosphorus-analogue 2D material with exceptionally large nonlinear optical response, high stability, and applications in all-optical switching and wavelength conversion," *Adv. Opt. Mater.*, vol. 6, no. 2, pp. 1700985–1700994, 2018.
- [29] R. Wu, Y. Zhang, S. Yan, et al., "Purely coherent nonlinear optical response in solution dispersions of graphene sheets," *Nano Lett.*, vol. 11, no. 12, pp. 5159–5164, 2011.
- [30] J. Zhang, F. Feng, Y. Pu, X. Li, C. H. Lau, and W. Huang, "Tailoring the porosity in iron phosphosulfide nanosheets to improve the performance of photocatalytic hydrogen evolution," *ChemSusChem*, vol. 12, no. 12, pp. 2651–2659, 2019.
- [31] Z. Lin, Y. Liu, U. Halim, et al., "Solution-processable 2D semiconductors for high-performance large-area electronics," *Nature*, vol. 562, no. 7726, pp. 254–258, 2018.
- [32] A. Ambrosi and M. Pumera, "Exfoliation of layered materials using electrochemistry," *Chem. Soc. Rev.*, vol. 47, no. 19, pp. 7213–7224, 2018.
- [33] W. Zhu, W. Gan, Z. Muhammad, et al., "Exfoliation of ultrathin FePS₃ layers as a promising electrocatalyst for the oxygen

- evolution reaction,” *Chem. Commun. Camb.*, vol. 54, no. 35, pp. 4481–4484, 2018.
- [34] C. C. Mayorga-Martinez, Z. Sofer, D. Sedmidubsky, S. Huber, A. Y. Eng, and M. Pumera, “Layered metal thiophosphite materials: magnetic, electrochemical, and electronic properties,” *ACS Appl. Mater. Int.*, vol. 9, no. 14, pp. 12563–12573, 2017.
- [35] X. Wang, K. Du, Y. Y. Fredrik Liu, et al., “Raman spectroscopy of atomically thin two-dimensional magnetic iron phosphorus trisulfide FePS₃ crystals,” *2D Mater.*, vol. 3, no. 3, pp. 031009–031018, 2016.
- [36] Y. Jia, Y. Liao, L. Wu, et al., “Nonlinear optical response, all optical switching, and all optical information conversion in NbSe₂ nanosheets based on spatial self-phase modulation,” *Nanoscale*, vol. 11, no. 10, pp. 4515–4522, 2019.
-
- Supplementary Material:** The online version of this article offers supplementary material (<https://doi.org/10.1515/nanoph-2020-0336>).