Solution Growth of Two-Dimensional Bi$_2$Se$_3$ Nanosheets for Two-Color All-Optical Switching

Xinghua Wu $^{1,2}$, Chao Tan $^3$, Qingkai Wang $^2$, Yanyan Guo $^1$, Dianyuan Wang $^2$, Yongqian Wang $^1$ and Dawei Meng $^1, *$

$^1$ Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, China; 51205879@163.com (X.W.); yyyguo_1980@163.com (Y.G.); cugwyq@126.com (Y.W.)
$^2$ College of Science, Key Laboratory for Microstructural Functional Materials of Jiangxi Province, Jiujiang University, Jiujiang 332005, China; 79792239@163.com (Q.W.); 1064532@163.com (D.W.)
$^3$ School of Information and Electrical Engineering, Hunan University of Science and Technology, Xiangtan 411201, China; chaotanhnu@163.com

* Correspondence: dwmeng@cug.edu.cn; Tel.: +86-027-6788-3731; Fax: +86-027-6788-3731

Received: 27 October 2017; Accepted: 18 November 2017; Published: 21 November 2017

Abstract: Two-dimensional Bi$_2$Se$_3$ nanosheets with hexagonal shape are synthesized by a solution synthetic route. The Bi$_2$Se$_3$ nanosheets are 120 nm in edge width and 7 nm in thickness. The size of the Bi$_2$Se$_3$ nanosheets can be controlled by choosing different kinds of reducing agents including hydroxylamine and ethylenediamine. Subsequently, we demonstrate a configuration of two-color all-optical switching based on plasma channels effect using the as-synthesized Bi$_2$Se$_3$ nanosheets as an optical media. The signal light can be modulated as two states including dot and ring shape by changing the intensity of control light. The modulated signal light exhibits excellent spatial propagation properties. As a type of interesting optical material, ultrathin two-dimensional Bi$_2$Se$_3$ nanosheets might provide an effective option for photoelectric applications.

Keywords: nanoparticles; optical materials and properties; nanocrystalline; optical switching

1. Introduction

Two-dimensional (2D) materials including graphene [1], transition metal dichalcogenides [2], topological insulators [3] and black phosphorus [4,5] have large lateral size, but small vertical thickness. Due to unique optical, electronic, physical and chemical properties, 2D materials have attracted much attention and have been widely applied in transistors, sensors, batteries, supercapacitors and solar cells [6]. As a 2D material, Bi$_2$Se$_3$ possesses excellent thermoelectric properties and novel electronic band structure, which are heavily dependent on its morphology and size. Considerable efforts have been made to synthesize well-defined Bi$_2$Se$_3$ nanostructures via physical vapor deposition [7], molecular beam epitaxy [8], mechanical exfoliation [9] and liquid phase exfoliation [10–15]. Solution-based synthesis is an excellent alternative for the preparation of high quality ultrathin 2D Bi$_2$Se$_3$ nanosheets [16–18] and has the advantages of simplicity, low reaction temperature, high yield and large amount [19–23]. The morphology and size of 2D Bi$_2$Se$_3$ nanosheets can be effectively modulated by changing reaction conditions including surfactants, pH value, reaction temperature and time [12,14,19,24,25]. The reducing agent is necessary and critical for the synthesis of 2D Bi$_2$Se$_3$ nanosheets. However, searching for an effective reducing agent and establishing the relationship between the reducing agent and the size of nanoparticles are serious challenges.

All-optical switching plays an important role in the all-optical signal processing and optical communication. The performances of all-optical switching heavily depend on optical materials and device configurations [26]. Compared to the traditional nonlinear optical materials, two-dimensional materials have great advantages owing to their strong light-matter interactions, broadband and
ultrafast optical responses, large third-order optical nonlinearity [17,27]. Based on spatial self-phase modulation (SSPM) effect, all-optical switching in MoS$_2$ and Bi$_2$Se$_3$ dispersion solution have been realized [26,28–32]. However, self-diffraction ring formation process is slow, and the SSPM pattern is unstable, hindering the application in ultrahigh-speed optical devices. In order to enhance the performance of the device, the search for another effective and reliable approach to realized all-optical switching based on 2D materials is always highly encouraged.

In this paper, we demonstrate the all-optical switching in 2D Bi$_2$Se$_3$ dispersion solution based on plasma channels effect induced by femtosecond lase. The ultra-thin 2D Bi$_2$Se$_3$ nanosheets have been successfully synthesized by solution method. The size of the Bi$_2$Se$_3$ nanosheets can be controlled by choosing different kinds of reducing agents. Using ethylenediamine instead of hydroxylamine as a reducing agent, the lateral size of the nanosheets increases from 100 to 500 nm. Subsequently, the as-synthesized Bi$_2$Se$_3$ nanosheets were used as optical media for two-color all-optical switching based on plasma channel effect induced by femtosecond lase. Meanwhile, the propagation properties of modulated signal beam with ring-shape in free space are investigated.

2. Material Preparation and Experimental Setup

2.1. Synthesis of Ultrathin Bi$_2$Se$_3$ Nanosheets

Bismuth triacetate (Bi(CH$_3$CO$_2$)$_3$, ≥99.99%), Sodium selenite (Na$_2$SeO$_3$, ≥99%), Hydroxylamine solution (NH$_2$OH, 50% in H$_2$O) were purchased from Sigma-Aldrich (Shanghai, China). Ethylene glycol (EG), Poly(vinyl pyrrolidone) (PVP, $M_W$ ≈ 40,000), Ethylenediamine (≥99.5%), Acetic acid glacial (analytical reagent) were purchased from Aladdin (Shanghai, China). Ethanol (analytical reagent) and Acetone (analytical reagent) were purchased from Xilong Chemical Reagent Co. (Shanghai, China). All the chemicals were used as received without further purification.

In a typical synthesis, 0.3 mmol Bi(CH$_3$CO$_2$)$_3$ and 0.4 g PVP were dissolved in 10 mL ethylene glycol in a 25 mL round-bottom flask. Subsequently, 0.45 mmol Na$_2$SeO$_3$ and 1 mL acetic acid glacial were added into the above solution which was kept stirring evenly until Na$_2$SeO$_3$ was fully dissolved and a clear solution was obtained. After that, the solution was heated to 170 °C, then a mixture of 1 mL hydroxylamine solution and 1 mL ethylene glycol were rapidly injected, and the solution immediately turned black indicating the formation of Bi$_2$Se$_3$ nanosheets. The reaction was sustained for 15 min at the above temperature of 170 °C, and then the heating mantle was removed to cool the mixture naturally. After addition of 20 mL acetone, the product was centrifuged at 80,000 rpm for 5 min. The supernatant was discarded and the precipitation was collected. The washing steps were repeated with acetone for two times, and the final product was dispersed in ethanol.

2.2. Material Characterizations

Field emission scanning electron microscopy (FESEM, Hitachi S4800, Hitachi Ltd., Tokyo, Japan) was employed to study the morphology of the products. The morphology and microstructure of the as-prepared Bi$_2$Se$_3$ samples were characterized by high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F20, FEI, Beaverton, OR, USA). The topography and thickness of the as-prepared Bi$_2$Se$_3$ samples were determined by atomic force microscope (AFM, Bruker, Multimode 8, Camarillo, CA, USA). The crystal structure of the as-prepared Bi$_2$Se$_3$ samples were investigated by X-ray diffraction using Cu Kα radiation ($\lambda = 1.541$ Å) (XRD, D8 ADVANCE, Bruker, Camarillo, CA, USA). Raman spectra of the as-prepared Bi$_2$Se$_3$ samples were recorded using confocal Raman spectrometer with $\lambda = 532$ nm at room temperature (WITec Alpha 300 R, Ulm, Baden-Württemberg, Germany).

2.3. Experimental Setup for Two-Color All-Optical Switching

Figure 1 has shown the schematic diagram of proposed two-color all-optical switching configuration. In this system, we use continuous wave He-Ne laser with a central wavelength of 632 nm.
3. Results and Discussion

The morphology of the products was investigated by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) as shown in Figure 2a–j. The FESEM image (Figure 2a) reveals that the as-synthesized Bi$_2$Se$_3$ nanosheet through solution method has a very high yield. The nanosheets have regular shape and size, and are predominantly hexagonal morphology. Figure 2d is a typical TEM image of a single Bi$_2$Se$_3$ nanosheet, which further demonstrates that the as-synthesized nanosheet has perfect hexagonal morphology, and the lateral width of the nanosheet is about 100 nm. In order to make a better analysis to the composition of the nanosheets, Figure 2b,c show energy dispersive X-ray spectroscopy (EDS) elemental mapping images of the samples. Both element Bi and Se have a uniform distribution. The selected area electron diffraction (SAED) pattern shown in Figure 2e can be indexed to a six-fold symmetry [0001] zone axis of the rhombohedral Bi$_2$Se$_3$. The diffraction spots correspond to the (T100), (01T0) and (0T10) facets of Bi$_2$Se$_3$ nanosheets, respectively [22–24,33,34]. The high-resolution TEM (HRTEM) image of the Bi$_2$Se$_3$ nanosheets in Figure 2f exhibits high-resolution lattice fringes. The lattice fringes individually correspond to the (T100) facet and (01T0) facet of Bi$_2$Se$_3$. The Fast Fourier Transform (FFT) electron diffraction pattern of the Bi$_2$Se$_3$ nanosheets is shown in the inset of Figure 2g. The FFT pattern indicates the (T100), (10T0)

**Figure 1.** Schematic diagram of proposed two-color all-optical switching configuration. M1, silver-coated plane mirror; A1 and A2, attenuators; BS1 and BS2, beam splitters; NM, nonlinear material (Bi$_2$Se$_3$ dispersion solution).
and (0100) facets of Bi2Se3 nanosheets. The FFT pattern are of six-fold symmetry and can be identified as the projection of the hexagonal Bi2Se3 reciprocal lattice in [0001] direction. In order to determine the thickness and width of the as-synthesized Bi2Se3 nanosheets, the atomic force microscopy (AFM) images were carried out. The hexagonal morphology of Bi2Se3 nanosheets is shown in Figure 2h, and the height profile is shown in Figure 2i, which respectively correspond to line1 and line2 in Figure 2h. It is clear that the ultrathin Bi2Se3 nanosheet has a thickness of about 7 nm and a uniform width of about 120 nm [13].

The X-ray diffraction (XRD) pattern of the as-synthesized Bi2Se3 nanosheets is shown in Figure 3a. All the diffraction peaks can be indexed to rhombohedral Bi2Se3 structure (space group: R3m), which are highly consistent with the literature values (JCPDS No. 33-0214) [13,15,35,36]. No peaks of Se or other alloy compounds were detected. Bi2Se3 is a layered material with a crystal structure of quintuple layers (QL) in which atoms are covalently bonded and stacked in a sequence of Se-Bi-Se-Bi-Se [37]. The QLs are bonded together by weak van der Waals interactions so that ultrathin 2D Bi2Se3 can be obtained by solution growth route [13,38]. Figure 3b shows the Raman spectrum of the as-synthesized Bi2Se3 nanosheets [39,40]. The spectrum contains three main peaks (at 70, 128 and 172 cm−1) which correspond to A11g, E2g and A21g modes, respectively [33]. E2g mode is in-plane vibrational mode, but A11g and A21g modes are out-of-plane vibrational modes. Out-of-plane vibrational modes are sensitive to the thickness and the intensity increases with reduced thickness [41,42]. The intensity of the A11g mode in the ultrathin 2D Bi2Se3 nanosheets is relatively strong due to ultrathin thickness of 2D nanosheets [43].

Figure 2. (a) Field emission scanning electron microscopy (FESEM) images of Bi2Se3 nanosheets; (b,c) EDS elemental mapping images showing the distribution of Bi and Se; (d) transmission electron microscopy (TEM) image of Bi2Se3 nanosheets; (e) the corresponding selected area electron diffraction (SAED) pattern; (f) the high-resolution transmission electron microscopy (HRTEM) image; (g) the Fast Fourier Transform (FFT) pattern; (h) atomic force microscope (AFM) image of the Bi2Se3 nanosheet; (i,j) AFM height profile corresponding to the line1 and line2 in (h).
very rapid. With all other reaction conditions unchanged, when the ethylenediamine instead of
hydroxylamine is rapidly injected into the precursor solution, the mixture solution first becomes dark
brown, then slowly becomes black, indicating that the reaction process is relatively slow. As shown
in Figure 4, the width of the Bi$_2$Se$_3$ nanosheets is about 100 nm for hydroxylamine, and the width is
about 700 nm for ethylenediamine.

The size of Bi$_2$Se$_3$ nanosheet is controllable by choosing different reducing agents including
hydroxylamine and ethylenediamine. During the preparation of Bi$_2$Se$_3$ nanosheet, when the
hydroxylamine is rapidly injected into the precursor solution, the mixture solution immediately
becomes black indicating that the Bi$_2$Se$_3$ nanosheet has been produced and the reaction process is
very rapid. With all other reaction conditions unchanged, when the ethylenediamine instead of
hydroxylamine is rapidly injected into the precursor solution, the mixture solution first becomes dark
brown, then slowly becomes black, indicating that the reaction process is relatively slow. As shown
in Figure 4, the width of the Bi$_2$Se$_3$ nanosheets is about 100 nm for hydroxylamine, and the width is
about 700 nm for ethylenediamine.

The reducibility of hydroxylamine is stronger than that of ethylenediamine. When the
hydroxylamine is injected into the precursor mixture solution, SeO$_5^-$ is reduced to Se$^{2-}$ which
combine with Bi$^{3+}$ to form a large number of crystal nuclei rapidly. The number of crystal nuclei
is so large that the growth of the crystal nuclei lacks sufficient power, resulting in the formation of
smaller Bi$_2$Se$_3$ nanosheets [23]. On the contrary, when the ethylenediamine is used, the nucleation rate
is slower and the number of crystal nuclei is smaller so that the crystal nuclei fully grow and larger
nanosheets are obtained.

Figure 5a–d shows the beam profiles of the signal light in the Bi$_2$Se$_3$ dispersion solution at the
concentration of 30 μg/mL under different power of control light beams ($P_{fs} = 0, 1.5, 3.4$, and 6 mW,
respectively). In order to further clarify the change of signal light intensity, Figure 5e gives the profile
of light intensity distribution through the center of signal light. When the intensities of the control
light is fixed at 0 mW, the signal light keeps its initial spatial intensity distribution as Gauss laser
intensity distribution through the center of signal light. When the intensities of the control

![Figure 3](image-url)  
**Figure 3.** (a) X-ray diffraction (XRD) pattern of the Bi$_2$Se$_3$ nanosheets; (b) Raman spectrum of Bi$_2$Se$_3$
anosheets. The inset is crystal structure and schematic diagram of the lattice vibrations.

![Figure 4](image-url)  
**Figure 4.** TEM images of Bi$_2$Se$_3$ nanosheets obtained from the reactions with different reducing agents:
(a) hydroxylamine; (b) ethylenediamine.
light is fixed at 0 mW, the signal light keeps its initial spatial intensity distribution as Gauss laser spot, and the optical switching is ON. As $P_{fs}$ increases continuously, the light beam collapses toward the center. The intensity of the light spot center decreases gradually, while the intensity of light spot edge increases gradually at the same time. When the control light increases to 6 mW, a dark spot arises in the center region of the signal light, and the optical switching is OFF. The signal light is modulated into a ring shape which remains stable. It can be attributed to laser plasma effect induced by the nonlinearly optical property of the Bi$_2$Se$_3$ nanosheets. When the control light passes through the Bi$_2$Se$_3$ dispersion solution, if the power of control light reaches the ionization threshold of the Bi$_2$Se$_3$ dispersion solution, the plasma channel will be produced. Since the intensity distribution of the control light is Gaussian, the gradient of the electron density and the refractive index distribution in the plasma channel is also approximately Gaussian. The electron density of the plasma in the center of the spot is very high, and the electron density at the edge is low. When the signal light beam passes through the plasma channel, the plasma channel will play the role of a graded-index diverging lens. The signal light beam focuses on the periphery of plasma channel and the intensity of signal light beam is zero in the center.

**Figure 5.** (a–d) Intensity profiles of signal beams under different $P_{fs}$; (e) Radial intensity distribution of signal beams under different $P_{fs}$.

Figure 6 shows the relationship between the dark spot size of signal beams (DSS) and power of control light beams ($P_{fs}$) in three Bi$_2$Se$_3$ dispersion solutions (30, 15, and 7.5 $\mu$g/mL). DSS is defined as the full width at half maximum of the dark spot in the center of signal light beam. In the same concentration of Bi$_2$Se$_3$, with the increase of power of control light, DSS gradually increase. Meanwhile, as the concentration of Bi$_2$Se$_3$ increases, to generate the same DSS, the required control light power will decrease. For example, in order to obtain DSS = 1.4 mm, the power of control light required for the Bi$_2$Se$_3$ dispersion solution with concentration of 30, 15, and 7.5 $\mu$g/mL is 4 mW, 5 mW and 6 mW respectively. It can be attributed to that when the concentration of Bi$_2$Se$_3$ increases, the nonlinear effect is enhanced and the control light power required for the generation of same plasma channels is lower. That is to say, it is easier to obtain more obvious switching effect in high concentration dispersion solution.
Figure 6. The relationship between the dark spot size (DSS) of signal beams and $P_{fs}$ in three Bi$_2$Se$_3$ dispersion solutions (30, 15, and 7.5 $\mu$g/mL in IPA).

To verify the stability of signal beam when the switching is OFF, we study the propagation properties of the signal beam in free space. The signal beam is modulated by the control light beam in the Bi$_2$Se$_3$ disperse solution to form dark spots. The distance between the Bi$_2$Se$_3$ dispersion solution and the CCD camera is set to distance D. When the CCD camera moves along the central axis of the signal beam, the distance D changes and a series of spatial intensity distribution patterns are obtained. Figure 7a shows the intensity distribution patterns of signal light beam generated in the Bi$_2$Se$_3$ dispersion solution (30 $\mu$g/mL) at different propagation distance (D) when $P_{fs}$ is 6 mW. With the increase of the distance D, the signal beam keeps initial spatial intensity distribution and exhibits favorable stability in free space.

In order to investigate the propagation of light beam in free space, we further investigated the FWHM of initial signal beam and DSS of modulated signal beam changing with distance D. When the intensities of the control light is 0 mW, the signal light keeps Gaussian intensity distribution, and the optical switching is ON, as shown in Figure 7b. The FWHM of initial signal light beam increases with the increase of distance D. The FWHM of the initial signal beams passing through the Bi$_2$Se$_3$ dispersion solution are larger than that through the water. The FWHM of the initial signal beam increases gradually with the increase of the concentration of Bi$_2$Se$_3$ dispersion solution.

Figure 7c displays the relationships between the dark spot size (DSS) of the modulated signal light beam and the propagation distance (D) at different solution concentrations when $P_{fs}$ is 6 mW and the optical switching is OFF. The DSS of the modulated signal beam increases gradually with the increase of distance D. Meanwhile, the DSS of the initial signal beam increases gradually with the increase of the concentration of Bi$_2$Se$_3$ dispersion solution. It is more easily to achieve control of signal light beam at high concentrations of Bi$_2$Se$_3$ dispersion solution.
Acknowledgments: The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 41472042, 41172051, 11664020 and 11647134), the Technology Project of Jiangxi Provincial Education Department (No. GJJ161066) and the Jiangxi Natural Science Foundation (Grant No. 20171BAB201017).

Author Contributions: Xinghua Wu and Chao Tan designed the experiments; Qinkai Wang contributed the materials; Xinghua Wu wrote the paper; Yanyan Guo, Dianyuan Wang, Yongqian Wang and Dawei Meng analyzed the data.

Conflicts of Interest: The authors declare no conflict of interest.

4. Conclusions

In summary, two-color all-optical switching has successfully been realized based on two-dimensional Bi$_2$Se$_3$ nanosheets as an optical media. Two-dimensional Bi$_2$Se$_3$ nanosheets with highly uniform hexagonal morphology have been successfully synthesized. Then, the as-synthesized Bi$_2$Se$_3$ nanosheets were dispersed into solution and innovatively used as an optical media for the realization of two-color all-optical switching. It is envisaged that two-dimensional Bi$_2$Se$_3$ nanomaterials may be utilized as an excellent optical media for all-optical processing toward practical applications, leading to the development of new photoelectric devices.

Acknowledgments: The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 41472042, 41172051, 11664020 and 11647134), the Technology Project of Jiangxi Provincial Education Department (No. GJJ161066) and the Jiangxi Natural Science Foundation (Grant No. 20171BAB201017).

Author Contributions: Xinghua Wu and Chao Tan designed the experiments; Qinkai Wang contributed the materials; Xinghua Wu wrote the paper; Yanyan Guo, Dianyuan Wang, Yongqian Wang and Dawei Meng analyzed the data.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Geim, A.K.; Novoselov, K.S. The rise of graphene. Nat. Mater. 2007, 6, 183–191. [CrossRef] [PubMed]
2. Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-layer MoS$_2$ transistors. Nat. Nanotechnol. 2011, 6, 147–150. [CrossRef] [PubMed]
3. Chen, Y.; Analytis, J.; Chu, J.-H.; Liu, Z.; Mo, S.-K.; Qi, X.-L.; Zhang, H.; Lu, D.; Dai, X.; Fang, Z. Experimental realization of a three-dimensional topological insulator, Bi$_2$Te$_3$. Science 2009, 325, 178–181. [CrossRef] [PubMed]
10. Nicolosi, V.; Chhowalla, M.; Kanatzidis, M.G.; Strano, M.S.; Coleman, J.N. Liquid Exfoliation of Layered

6. Tan, C.; Cao, X.; Wu, X.-J.; He, Q.; Yang, J.; Zhang, X.; Chen, J.; Zhao, W.; Han, S.; Nam, G.-H.; et al. Recent Advances in Ultrathin Two-Dimensional Nanomaterials. Chem. Rev. 2017, 117, 6225–6331. [CrossRef] [PubMed]

7. Cao, H.; Venkatasubramanian, R.; Liu, C.; Pierce, J.; Yang, H.; Hasan, M.Z.; Wu, Y.; Chen, Y.P. Topological insulator Bi$_2$Te$_3$ films synthesized by metal organic vapor deposition. Appl. Phys. Lett. 2012, 101, 162104. [CrossRef]

8. Chen, X.; Ma, X.-C.; He, K.; Jia, J.-F.; Xue, Q.-K. Molecular Beam Epitaxial Growth of Topological Insulators. Adv. Mater. 2011, 23, 1162–1165. [CrossRef] [PubMed]

9. Goyal, V.; Teweldebrhan, D.; Balandin, A.A. Mechanically-exfoliated stacks of thin films of Bi$_2$Te$_3$ topological insulators with enhanced thermoelectric performance. Appl. Phys. Lett. 2010, 97, 133117. [CrossRef]

10. Nicolosi, V.; Chhowalla, M.; Kanatzidis, M.G.; Strano, M.S.; Coleman, J.N. Liquid Exfoliation of Layered Materials. Science 2013, 340. [CrossRef]

11. Xu, H.M.; Chen, G.; Jin, R.C.; Chen, D.H.; Wang, Y.; Pei, J. Green synthesis of Bi$_2$Se$_3$ hierarchical nanostructure and its electrochemical properties. RSC Adv. 2014, 4, 8922–8929. [CrossRef]

12. Min, Y.; Moon, G.D.; Kim, B.S.; Lim, B.; Kim, J.S.; Kang, C.Y.; Jeong, U. Quick, Controlled Synthesis of n-Type Nanostructured Thermoelectric Materials Prepared from Chemically Synthesized Ultrathin Bi$_2$Te$_3$ Nanoplatelets. Nano Lett. 2011, 11, 2407–2414. [CrossRef] [PubMed]

13. Hong, S.S.; Kundhikanjana, W.; Cha, J.J.; Lai, K.; Kong, D.; Meister, S.; Kelly, M.A.; Shen, Z.-X.; Cui, Y. Ultrathin topological insulator Bi$_2$Se$_3$ nanoribbons exfoliated by atomic force microscopy. Nano Lett. 2010, 10, 3118–3122. [CrossRef] [PubMed]

14. Chen, S.; Zhao, C.; Li, Y.; Huang, H.; Lu, S.; Zhang, H.; Wen, S. Broadband optical and microwave nonlinear response in topological insulator. Opt. Mater. Express 2014, 4, 587–596. [CrossRef]

15. Lu, S.; Zhao, C.; Zou, Y.; Chen, S.; Chen, Y.; Li, Y.; Zhang, H.; Wen, S.; Tang, D. Third order nonlinear optical property of Bi$_2$Se$_3$. Opt. Express 2013, 21, 2072–2082. [CrossRef] [PubMed]

16. Zhao, C.; Zhang, H.; Qi, X.; Chen, Y.; Wang, Z.; Wen, S.; Tang, D. Ultra-short pulse generation by a topological insulator based saturable absorber. Appl. Phys. Lett. 2012, 101, 211106. [CrossRef]

17. Son, J.S.; Choi, M.K.; Han, M.-K.; Park, K.; Kim, J.-Y.; Lim, S.J.; Oh, M.; Kuk, Y.; Park, C.; Kim, S.-J. n-Type Nanostructured Thermoelectric Materials Prepared from Chemically Synthesized Ultrathin Bi$_2$Te$_3$ Nanoplatelets. Nano Lett. 2012, 12, 640–647. [CrossRef] [PubMed]

18. Mi, J.-L.; Lock, N.; Sun, T.; Christensen, M.; Sondergaard, M.; Hald, P.; Hng, H.H.; Ma, J.; Iversen, B.B. Biomolecule-Assisted Hydrothermochromic Synthesis and Self-Assembly of Bi$_2$Te$_3$ Nanostring-Cluster Hierarchical Structure. ACS Nano 2010, 4, 2523–2530. [CrossRef] [PubMed]

19. Liu, X.; Fang, Z.; Zhang, Q.; Huang, R.; Lin, L.; Ye, C.; Ma, C.; Zeng, J. Ethylenediaminetetraacetic acid-assisted synthesis of Bi$_2$Se$_3$ nanostripes with unique edge sites. Nano Res. 2016, 9, 2707–2714. [CrossRef]

20. Liu, X.; Zhang, Y.; Li, J.; Lin, L.; Qian, Y.; Wang, Y.; Ye, C.; Ma, C.; Zeng, J. One-pot synthesis of Bi$_2$Se$_3$ nanostructures with rationally tunable morphologies. Nano Res. 2015, 8, 3612–3620. [CrossRef]

21. Ota, J.R.; Roy, P.; Srivastava, S.K.; Popovitz-Biro, R.; Tenne, R. A simple hydrothermal method for the growth of Bi$_2$Se$_3$ nanorods. Nanotechnology 2006, 17, 1700–1705. [CrossRef] [PubMed]
26. Zheng, J.; Yang, Z.; Si, C.; Liang, Z.; Chen, X.; Cao, R.; Guo, Z.; Wang, K.; Zhang, Y.; Ji, J.; et al. Black Phosphorus Based All-Optical-Signal-Processing: Toward High Performances and Enhanced Stability. *ACS Photonics* 2017, 4, 1466–1476. [CrossRef]

27. Lu, S.; Ge, Y.; Sun, Z.; Huang, Z.; Cao, R.; Zhao, C.; Wen, S.; Fan, D.; Li, J.; Zhang, H. Ultrafast nonlinear absorption and nonlinear refraction in few-layer oxidized black phosphorus. *Photonics Res.* 2016, 4, 286. [CrossRef]

28. Wu, Y.; Wu, Q.; Sun, F.; Cheng, C.; Meng, S.; Zhao, J. Emergence of electron coherence and two-color all-optical switching in MoS2 based on spatial self-phase modulation. *Proc. Natl. Acad. Sci. USA* 2015, 112, 11800–11805. [CrossRef] [PubMed]

29. Li, X.; Liu, R.; Xie, H.; Zhang, Y.; Lyu, B.; Wang, P.; Wang, J.; Fan, Q.; Ma, Y.; Tao, S.; et al. Tri-phase all-optical switching and broadband nonlinear optical response in Bi2Se3 nanosheets. *Opt. Express* 2017, 25, 18346–18354. [CrossRef] [PubMed]

30. Xu, Y.; Wang, W.; Ge, Y.; Guo, H.; Zhang, X.; Chen, S.; Deng, Y.; Lu, Z.; Zhang, H. Stabilization of Black Phosphorous Quantum Dots in PMMA Nanofiber Film and Broadband Nonlinear Optics and Ultrafast Photons Application. *Adv. Funct. Mater.* 2017, 27, 1702437. [CrossRef] [PubMed]

31. Li, X.; Hu, K.; Lyu, B.; Zhang, J.; Wang, Y.; Wang, P.; Xiao, S.; Gao, Y.; He, J. Enhanced Nonlinear Optical Response of Rectangular MoS2 and MoS2/TiO2 in Dispersion and Film. *J. Phys. Chem. C* 2016, 120, 18243–18248. [CrossRef]

32. Shi, B.; Miao, L.; Wang, Q.; Du, J.; Tang, P.; Liu, J.; Zhao, C.; Wen, S. Broadband ultrafast spatial self-phase modulation for topological insulator Bi2Te3 dispersions. *Appl. Phys. Lett.* 2015, 107, 151101. [CrossRef]

33. Zhuang, A.; Zhao, Y.; Liu, X.; Xu, M.; Wang, Y.; Jeong, U.; Wang, X.; Zeng, J. Controlling the lateral and vertical dimensions of Bi2Se3 nanobelts via seeded growth. *Nano Res.* 2014, 8, 246–256. [CrossRef]

34. Min, Y.; Park, G.; Kim, B.; Giri, A.; Zeng, J.; Roh, J.W.; Kim, S.I.; Lee, K.H.; Jeong, U. Synthesis of Multi-Shell Nanoplates by Consecutive Epitaxial Growth of Bi2Se3 and Bi2Te3 Nanoplates and Enhanced Thermoelectric Properties. *ACS Nano* 2015, 9, 6843–6853. [CrossRef] [PubMed]

35. Kong, D.; Dang, W.; Cha, J.J.; Li, H.; Meister, S.; Peng, H.; Liu, Z.; Cui, Y. Few-layer nanoplates of Bi2Se3 and Bi2Te3 with highly tunable chemical potential. *Nano Lett.* 2010, 10, 2245–2250. [CrossRef] [PubMed]

36. Steinberg, H.; Gardner, D.R.; Lee, Y.S.; Jarillo-Herrero, P. Surface state transport and ambipolar electric field effect in Bi2Se3 nanodevices. *Nano Lett.* 2010, 10, 5032–5036. [CrossRef] [PubMed]

37. Ambrosi, A.; Sofer, Z.; Luxa, J.; Pumera, M. Exfoliation of Layered Topological Insulators Bi2Se3 and Bi2Te3 via Electrochemistry. *ACS Nano* 2016, 10, 11442–11448. [CrossRef] [PubMed]

38. Wang, D.; Yu, D.; Mo, M.; Liu, X.; Qian, Y. Preparation and characterization of wire-like Sb2Se3 and flake-like Bi2Se3 nanocrystals. *J. Cryst. Growth* 2003, 253, 445–451. [CrossRef]

39. Yuan, J.; Zhao, M.; Yu, W.; Lu, Y.; Chen, C.; Xu, M.; Li, S.; Loh, K.P.; Bao, Q. Raman Spectroscopy of Two-Dimensional Bi(3)TeSe(3) platelets Produced by Solvothermal Method. *Materials* 2015, 8, 5007–5017. [CrossRef] [PubMed]

40. Shahil, K.M.F.; Hossain, M.Z.; Goyal, V.; Balandin, A.A. Micro-Raman spectroscopy of mechanically exfoliated few-quintuple layers of Bi2Te3, Bi2Se3, and Sb2Te3 materials. *J. Appl. Phys.* 2012, 111, 054305. [CrossRef] [PubMed]

41. Jana, M.K.; Biswas, K.; Rao, C.N. Ionothermal synthesis of few-layer nanostructures of Bi2Se3 and related materials. *Chemistry* 2013, 19, 9110–9113. [CrossRef] [PubMed]

42. Dang, W.; Peng, H.; Li, H.; Wang, P.; Liu, Z. Epitaxial heterostructures of ultrathin topological insulator nanoplate and graphene. *Nano Lett.* 2010, 10, 2870–2876. [CrossRef] [PubMed]

43. Dun, C.; Hewitt, C.A.; Huang, H.; Xu, J.; Montgomery, D.S.; Nie, W.; Jiang, Q.; Carroll, D.L. Layered Bi2Se3 nanoplate/polyvinylidene fluoride composite based n-type thermoelectric fabrics. *ACS Appl. Mater. Interfaces* 2015, 7, 7054–7059. [CrossRef] [PubMed]

© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).