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Complete List of Authors:	Chitara, Basant; North Carolina Central University, Chemistry and Biochemistry Limbu, Tej; North Carolina Central University, Chemistry and Biochemistry Orlando, Jason; North Carolina Central University, Chemistry and Biochemistry Tang, Yongan ; North Carolina Central University, Department of Mathematics and Physics Yan, Fei; North Carolina Central University, Chemistry and Biochemistry

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*Basant Chitara, Tej B. Limbu, Jason D. Orlando, Yongan Tang, and Fei Yan**

Dr. B. Chitara, Dr. T. B. Limbu, J. D. Orlando, Prof. F. Yan
Department of Chemistry and Biochemistry, North Carolina Central University, Durham, NC
27707, USA

Email: chitara.basant@gmail.com, fyan@ncsu.edu

Prof. Y. Tang

Department of Mathematics and Physics, North Carolina Central University, Durham, NC
27707, USA

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Recently, a zipper two-dimensional (2D) material Bi₂O₂Se belonging to layered bismuth oxychalcogenide (Bi₂O₂X: X = S, Se, Te) family, has emerged as an alternate candidate to van der Waals 2D materials for high-performance electronic and optoelectronic applications. This hints towards exploring the other members of the Bi₂O₂X family for their true potential and bismuth oxysulfide (Bi₂O₂S) could be the next member for such applications. Here, we demonstrate for the first time, the scalable room-temperature chemical synthesis and near-infrared (NIR) photodetection of ultrathin Bi₂O₂S nanosheets. The thickness of the freestanding nanosheets was around 2 - 3 nm with a lateral dimension of ~ 80 - 100 nm. Solution-processed NIR photodetector was fabricated from ultrathin Bi₂O₂S nanosheets. The photodetector showed high performance, under 785 nm laser illumination, with a photoresponsivity of 4 A/W, an external quantum efficiency of 630%, and a normalized photocurrent-to-dark-current ratio of 1.3×10^{10} per watt with a fast response time of 100 ms. Taken together, the findings suggest that Bi₂O₂S nanosheets could be a promising alternative 2D material for next-generation large-area flexible electronic and optoelectronic devices.

Introduction

Infrared (IR) photodetectors find a myriad of applications in thermal imaging, biomedical imaging, night vision, information communication, and military etc.¹⁻³ The specific wavelength of detection is achieved by choosing materials with desirable bandgaps. Silicon⁴ and germanium⁵ have been commercialized for near-infrared (NIR) photodetection for a long time. However, these materials cannot be used for bendable and flexible optoelectronics.⁶ Therefore, there is a continuous thrust for finding new materials with high mechanical strength, tunable bandgap, high absorption and relative ease of availability to be processed as flexible substrates for IR photodetection. 2D materials offers excellent electronic^{1,7-9} and mechanical properties,¹⁰⁻¹² thus fulfilling aforementioned prerequisites for large-area and low-cost IR photodetecting applications. Following this, several IR photodetectors have been fabricated from graphene,¹ transition metal dichalcogenides (TMDs),^{3,13} black phosphorus (BP),¹⁴⁻¹⁹ and MXenes.²⁰ However, graphene suffers from the absence of bandgap and low light absorption,^{1,17} TMDs, BP, and MXenes require complex encapsulation^{18,19} and/or functionalization²⁰, which prompts further exploration of alternative 2D materials for such applications.

Recently, a new 2D air-stable bismuth oxyselenide²¹⁻²⁵ ($\text{Bi}_2\text{O}_2\text{Se}$) owing to its extremely high carrier mobility ($>20,000 \text{ cm}^2/\text{Vs}$ at 2 K), low effective mass ($0.14 m_0$) and bandgap tunability has revolutionized the research in bismuth oxychalcogenides ($\text{Bi}_2\text{O}_2\text{X}$: X = S, Se, Te) family, which is in complementary to van der Waals (vdW) 2D materials for high-performance electronic and optoelectronic applications. $\text{Bi}_2\text{O}_2\text{X}$ have been extensively studied for their thermoelectric properties and few research has been devoted to electronic²¹ and optoelectronic properties.^{24,26-29} However, in all of the aforementioned studies highlighting $\text{Bi}_2\text{O}_2\text{Se}$, it has been obtained by synthesis techniques such as chemical vapor deposition (CVD), physical

vapor deposition and crystal growth methods requiring high temperature. Moreover, $\text{Bi}_2\text{O}_2\text{Se}$ contains selenium which is highly toxic in nature.³⁰ Thus, it would be interesting to explore $\text{Bi}_2\text{O}_2\text{S}$, another member belonging to the same family which is selenium-free and offers possibility of room-temperature synthesis. $\text{Bi}_2\text{O}_2\text{S}$ has an orthorhombic crystal structure with a space group of Pnm.³¹ It exhibits a bandgap of 1.5 eV, and possesses efficient charge dissociation, high charge carrier transport and long carrier lifetime.^{32–34} The one key aspect of these layered 2D materials making them different from vdW 2D materials is the presence of weak interlayer interaction in contrast to vdW interaction. $\text{Bi}_2\text{O}_2\text{S}$ loosely packed structure can be exploited in photocatalytic and photovoltaic applications.^{35,36} Moreover, $\text{Bi}_2\text{O}_2\text{S}$ has been predicted to exhibit ferroelectricity/ferroelasticity.³⁷ Therefore, $\text{Bi}_2\text{O}_2\text{S}$ provides a unique combination of semiconducting properties with ferroelectric/ferroelastic properties for next-generation electronic and optoelectronic devices. In the present investigation, ultrathin freestanding $\text{Bi}_2\text{O}_2\text{S}$ nanosheets have been synthesized at room temperature in contrast to hydrothermal and chemical bath deposition reported in literature.^{31–33,35,36} While both methods have the ability to grow large and good quality crystals, the hydrothermal synthesis method suffers from certain drawbacks such as needing expensive autoclaves and high temperature and the difficulty of observing the crystal growth in real time, and the chemical bath deposition takes hours to complete and is not able to produce mono- or few-layered $\text{Bi}_2\text{O}_2\text{S}$ nanosheets. Hence there is a need for a simple yet cost-effective method for producing a thermodynamically stable suspension of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets at ambient conditions. In this study, $\text{Bi}_2\text{O}_2\text{S}$ nanosheets was synthesized at room temperature via a one-pot wet-chemical synthetic method. Specifically, bismuth nitrate or $\text{Bi}(\text{NO}_3)_3$ was used as the Bi source, and thiourea (CH_4N_2) was chosen as the S source. The reaction was conducted under basic conditions in the presence of hydrazine. The low-cost room-temperature synthesis of freestanding $\text{Bi}_2\text{O}_2\text{S}$ nanosheets with high yield can be readily employed for large-area device applications, which is independent of the substrate in comparison to nanosheets grown over substrates.

Experimental

100 mg (0.206 mmol) of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 7.84 mg (0.103 mmol) of $\text{CH}_4\text{N}_2\text{S}$, 1 ml hydrazine hydrate and 306.8 mg (0.824 mmol) of disodium EDTA were used as the starting chemicals. 100 mg (0.206 mmol) of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 20 ml of water by sonication, producing a transparent solution. 1 ml of hydrazine hydrate was added to a separate vial containing $\text{CH}_4\text{N}_2\text{S}$ (12.7 mg). Finally, 120 mg of KOH and 320 mg of NaOH were added into the solution and were left overnight to obtain brown color precipitates. The product was then washed with water and dried in a desiccator overnight. The X-ray diffraction data was collected using Panalytical X'Pert PRO MRD HR XRD System. HORIBA LabRAM Evolution RAMAN Microscope-Smart SPM Atomic Force Microscope was used to obtain Raman spectra of $\text{Bi}_2\text{O}_2\text{S}$ samples with a 633 nm laser. Also, AFM image was obtained under the same instrument. The UV-Vis-NIR absorption spectrum of the synthesized nanosheets were obtained by employing UV 3000 spectrophotometer. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies were performed under an FEI Verios 460L SEM, and an FEI Tecnai T12 G2 TWIN TEM operating at 120 kV. The photo detecting device was fabricated by thermally evaporating Ti (5 nm)/Au (200 nm) over pre-cleaned Si/SiO₂ with 285 nm of oxide layer using shadow mask. The distance between the two electrodes was around 10 μm with \sim 1.3 mm width. $\text{Bi}_2\text{O}_2\text{S}$ nanosheets dispersed in water (3 mg/ml) using sonication, were drop-casted over the electrodes and dried overnight in vacuum. The thickness of the $\text{Bi}_2\text{O}_2\text{S}$ nanosheet film was around 1 μm as measured using a Dektak 150 stylus profilometer (Fig. S1, supplementary information) and AFM (Figs. S2, supplementary information). The current-voltage characteristics of the device was measured using Keysight B2902A Precision Source/Measure Unit. HORIBA LabRAM Evolution RAMAN Microscope-Smart SPM Atomic Force Microscope equipped with 532 nm, 633 nm and 785 nm laser was used as the light source in the present study. The intensity of the laser was calculated using a calibrated Si

photodiode. The difference between the current under illumination and the dark corresponds to the photocurrent.

Results and discussion

The scalable room-temperature synthesis of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets was carried out by reacting $\text{Bi}(\text{NO}_3)_3$ in water and thiourea in hydrazine hydrate, respectively. Eqs. 1 and 2 show the chemical reactions involved in the formation of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets. In the first step, $\text{Bi}(\text{NO}_3)_3$ undergoes hydrolysis to produce BiONO_3 and the hydrolysis process is expedited in alkaline medium. In the second step, S^{2-} resulting from the decomposition of thiourea interacts with BiONO_3 to form $\text{Bi}_2\text{O}_2\text{S}$, and the self-assembly of oppositely charged $(\text{Bi}_2\text{O}_2)^{2+}$ and S^{2-} layers results in the formation of ultrathin $\text{Bi}_2\text{O}_2\text{S}$ nanosheets, which is precipitated as a dark brown color product in the aqueous medium.

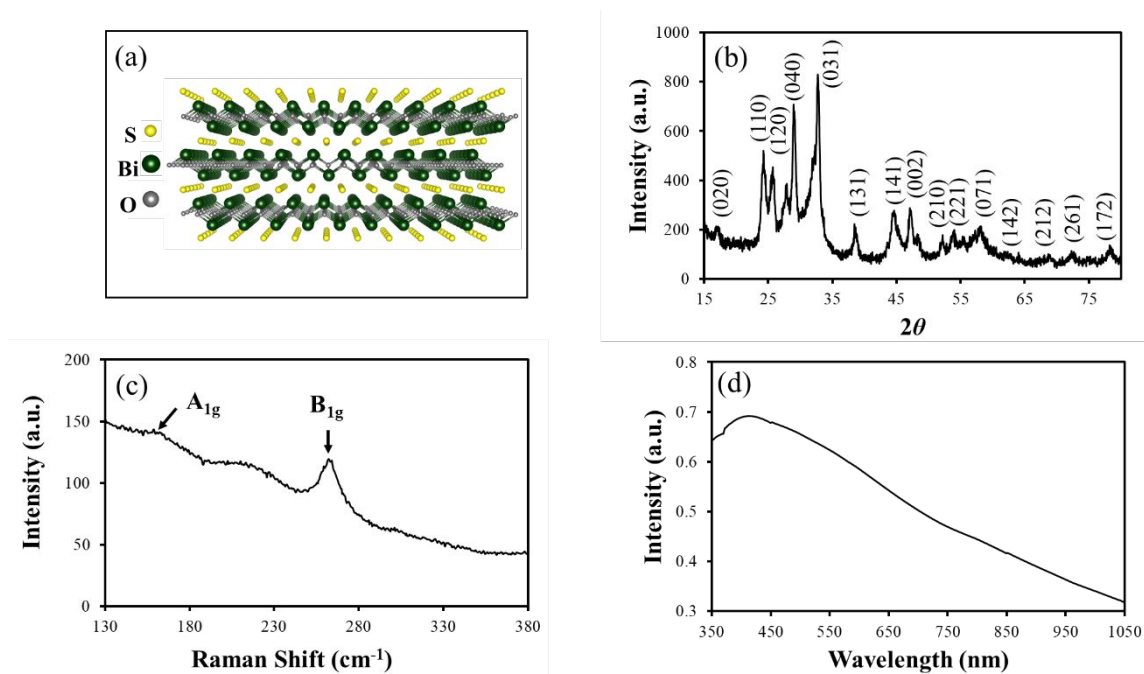


Fig. 1 (a) Crystal structure of $\text{Bi}_2\text{O}_2\text{S}$.³⁸ (b) XRD pattern of vacuum dried $\text{Bi}_2\text{O}_2\text{S}$ nanosheets. (c) Raman spectrum of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets. (d) UV-VIS-NIR absorption spectrum of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets.

Fig. 1a illustrates the crystal structure $\text{Bi}_2\text{O}_2\text{S}$ having alternating stacks of $[\text{Bi}_2\text{O}_2]_n^{2n+}$ and S_n^{2n-} layers, manifesting as weak interlayer interaction.³⁹ Fig. 1b demonstrates the typical XRD pattern of vacuum-dried $\text{Bi}_2\text{O}_2\text{S}$ nanosheets³¹ corresponding to the orthorhombic Pnm space group (JCPDS no.34-1493). Vacuum drying of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets leads to agglomeration of the nanosheets giving rise to clear peaks in the XRD pattern.⁴⁰ Fig. 1c displays the Raman spectrum of ultrathin $\text{Bi}_2\text{O}_2\text{S}$ nanosheet acquired using 633 nm laser showing theoretically predicted Raman peaks around at 164 cm^{-1} (A_g mode) and 263 cm^{-1} (B_{1g} mode).⁴¹ The broad hump around 217 cm^{-1} is due to the underlying Si/SiO₂ substrate. The UV-Vis-NIR absorption spectrum of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets is shown in Fig. 1d. The spectrum exhibits an absorption edge near 1000 nm, corresponding to an intrinsic bandgap absorption edge around 1.5 eV, which is in excellent agreement with what has been previously reported in literature.^{31,33,34}

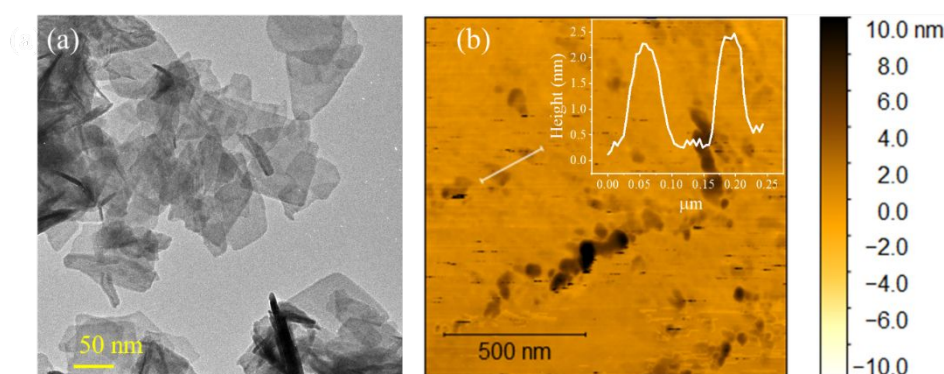


Fig. 2 (a) TEM image of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets. Scale bar: 50 nm. (b) AFM image of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets with corresponding height profile as an inset. Scale bar: 500 nm

In Fig. 2a, we show a TEM image of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets confirming the nanosheet morphology with crumpled nanosheets due to the weak electrostatic interaction between the layers. The AFM image of the $\text{Bi}_2\text{O}_2\text{S}$ nanosheets with corresponding height profile (inset) is shown in Fig. 2b. The lateral dimension of the $\text{Bi}_2\text{O}_2\text{S}$ nanosheets was around of 80-200 nm with a thickness of $\sim 2\text{-}3\text{ nm}$ corresponding to 2-3 layers, thus confirming the ultrathin nature of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets.

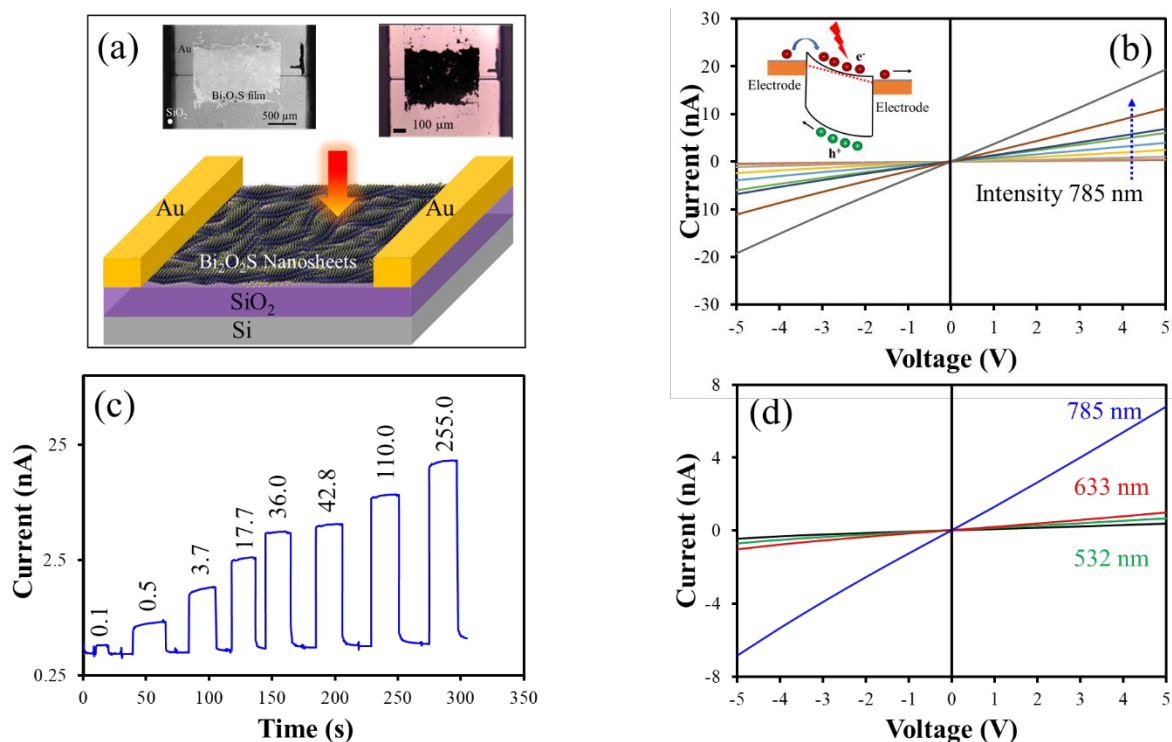


Fig. 3 (a) Schematic of photodetection device. Inset: SEM image of the device (left) and optical image of the device (right). (b) I-V characteristics of Bi₂O₂S nanosheets device in dark and under different illumination intensities at 785 nm. The inset shows the mechanism behind the detection. (c) Transient photoresponse of the device under different illumination of 785 nm at 5 V. The values in inset represents the intensity in mW/cm². (d) I-V characteristics of the device under dark, 532 nm, 633 nm and 785 nm with the light intensity of 40 mW/cm².

To further demonstrate the feasibility of solution-processed ultrathin Bi₂O₂S nanosheets for photodetection, we fabricated a two-terminal NIR photodetecting device by drop-casting, as shown in Fig. 3a. We examine the current-voltage (I-V) characteristics of the device in dark and under 785 nm with varying light intensity. As illustrated in Fig. 3b, the linear I-V indicates the ohmic contact between electrodes and Bi₂O₂S nanosheets. The mechanism behind the photodetection is presented as inset in Fig. 3b. Upon illuminating the device with NIR light source, the absorption of the NIR light generates electron-hole pairs,^{3,22,42} which in turn can be extracted on applying bias voltage across the device. The photoresponse in a photoconductor comprises of photoconductive response (fast response at low intensity) and bolometric response

(slow response at high intensity).²⁷ We have considered the photoconductive response to be the major contributor which is evident from the fast variation of photocurrent vs. illumination intensity. Fig. 3c depicts the current vs. time response of the device with different intensities of the 785 nm. The photocurrent was measured at 5 V with the NIR source being switched on and off, showing the reproducibility as well as transient response. The variation of photocurrent vs. illumination intensity showing that electrical conductivity of the device increases with increasing light intensity due to the absorption of more photons resulting in a larger photocurrent. To confirm the selectivity of the photodetectors, we have tested the device under 785 nm, 633 nm and 532 nm illumination with 40 mW/cm² (Fig. 3d). We can clearly see from Fig. 3d that the photoresponse is dependent on the wavelength of the illumination source. This could be attributed to the fact that the bandgap of the Bi₂O₂S nanosheets is around 1.5 eV, i.e. closer to 785 nm rather than 633 nm and 532 nm.

The applicability of these solution-processed photodetecting devices demands their photoresponsivity and external quantum efficiency to be high, the two important parameters for commercial photodetector applications.^{3,43,44} The photoresponsivity is defined corresponding to photocurrent generated per unit power of the incident light and the external quantum efficiency (EQE), i.e. the number of electrons detected per incident photon can be calculated as $R_\lambda = I_\lambda / P_\lambda S$, $EQE = hcR_\lambda / e\lambda$ respectively, where I_λ corresponds to photocurrent ($I_{\text{light}} - I_{\text{dark}}$), P_λ the intensity of light, S the device effective area under illumination, h Planck's constant, e the electronic charge, c the velocity of the light, λ the illumination wavelength. Normalized photocurrent-to-dark-current ratio (NPDR)^{45,46} derived from the ratio of the responsivity to the dark current, was also calculated for the device.

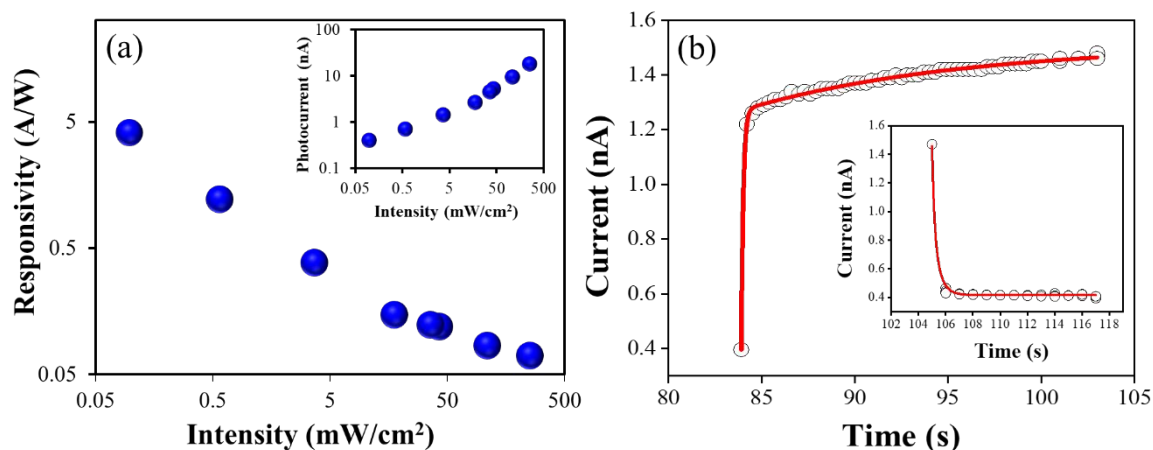


Fig. 4 (a) Photoresponsivity vs. intensity with photocurrent as a function of light intensity shown as inset. (b) Transient time response of photocurrent growth and decay (inset) for $\text{Bi}_2\text{O}_2\text{S}$ nanosheets photodetector. The open circles are the experimental data points and the solid lines are a fit to the equation.

The photoresponsivity of the devices decreases with increasing intensity as the responsivity is inversely proportional to the laser intensity (Fig. 4a).⁴⁷ The inset in Fig. 4a corresponds to increased photocurrent vs. illumination intensity as explained earlier. Another parameter deciding the applicability of the photo detecting device in practical application is the response and recovery time of the photodetector (Fig. (4b)). The time constants for photocurrent growth and decay can be estimated by the equations $I(t) = I_{\text{dark}} + A [1 - \exp(-(t-t_0)/\tau_1)] + B [1 - \exp(-(t-t_0)/\tau_2)]$ and $I(t) = I_{\text{dark}} + A [\exp(-(t-t_0)/\tau_1)] + B [\exp(-(t-t_0)/\tau_2)]$ respectively, where I_{dark} is dark current, τ is the time constant, t_0 corresponds to IR switch on and off time, A and B are scaling constants. In Fig. 4b, the red line shows the fitting over experimental data (open circles). The photocurrent rises rapidly in 100 ms followed by a slower component where the photocurrent takes nearly 11 s before saturation. During photocurrent decay, the current drops quickly within 160 ms, further taking 488 ms to reach its initial value. Our device exhibited a photoresponsivity

of 4 A/W, an EQE of 630 % and an NPDR of 1.3×10^{10} per watt. We have compared the photodetection performance of our device with other 2D materials as depicted in Table 1.

Table 1. Performance of 2D materials-based photodetectors.

2D Material	Synthesis Technique	Responsivity (A/W)	Response Time (ms)	Detection Range	NPDR (/W)	Reference
Graphene	Exfoliation	6×10^{-3}	6×10^{-8}	UV-SWIR	-	48
MoS ₂	Exfoliation	2570	2	Visible	2.5×10^{14}	49
Black P	Exfoliation	1.5	0.02	NIR	7.5×10^6	50
GaSe	Exfoliation	2.8	20	UV	2.3×10^9	42
MoTe ₂	Exfoliation	6	0.1	NIR	3.0×10^8	13
Bi ₂ O ₂ Se	CVD	2000	-	Visible	7.0×10^{11}	28
Bi ₂ O ₂ Se	CVD	3.5×10^4	0.30	Visible	3.5×10^{10}	43
Bi ₂ S ₃	Solvothermal	4.4	0.01	Vis-NIR	2.2×10^7	51
Bi ₂ Se ₃	CVD	23.8	540	NIR	2.4×10^9	52
Bi ₂ O ₂ S	RT wet chemical	4	100	NIR	1.3×10^{10}	This work

As evident from the Table 1, the photodetection performance of our Bi₂O₂S nanosheets photodetector is comparable to those fabricated from graphene,⁴⁸ black phosphorus,⁵⁰ GaSe,⁴² MoTe₂,¹³ Bi₂S₃,⁵¹ Bi₂Se₃⁵² and lower than that of MoS₂⁵³ and Bi₂O₂Se^{28,43}. The biggest advantage of our approach is the room-temperature synthesis method in comparison to CVD growth or high temperature methods to obtain crystal needed for exfoliation. In the present study, the room-temperature growth offers low cost and the possibility of fabrication of large area devices. The device showed excellent stability even after exposure to air for a month indicating the air stability of Bi₂O₂S nanosheets.

It is worth noting that the present investigation shows the measurement performed on a single device. However, the goal of this study is to highlight the new room-temperature synthesis method for obtaining Bi₂O₂S nanosheets. Photodetection has already been demonstrated in hydrothermally grown Bi₂O₂S^{32, 35}. It is anticipated that there will be small variation in device performance associated with drop-casting method owing to varied nanosheet density and thickness of the film. Further optimization of the reproducibility or photoresponsivity can be accomplished by other thin-film deposition techniques such as spin coating, spray coating, and inkjet printing etc.^{54,55}

Conclusions

To summarize, we demonstrate for the first time, a facile synthesis of freestanding Bi₂O₂S nanosheets under ambient conditions. The nanosheets were ultrathin with a thickness of around 2-3 nm. The synthesis method produces high yield air-stable nanosheets. Under 785 nm laser illumination, the solution-processed photodetector based on Bi₂O₂S nanosheets showed high performance with a photoresponsivity of 4 A/W, an external quantum efficiency of 630 %, and an NPDR of 1.3×10^{10} per watt. Therefore, this study puts forward air stable Bi₂O₂S nanosheets in conjugation with other 2D materials for exploitation in future flexible optoelectronics over large areas.

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References

- 1 C.-H. Liu, Y.-C. Chang, T. B. Norris and Z. Zhong, *Nat. Nanotechnol.*, 2014, **9**, 273–278.
- 2 F. Wang, Y. Zhang, Y. Gao, P. Luo, J. Su, W. Han, K. Liu, H. Li and T. Zhai, *Small*, 2019, **15**, 1901347.
- 3 Z. Yin, H. Li, H. Li, L. Jiang, Y. Shi, Y. Sun, G. Lu, Q. Zhang, X. Chen and H. Zhang, *ACS Nano*, 2012, **6**, 74–80.
- 4 M. W. Geis, S. J. Spector, M. E. Grein, J. U. Yoon, D. M. Lennon and T. M. Lyszczarz, *Opt. Express*, 2009, **17**, 5193–5204.
- 5 H. H. Tseng, H. Li, V. Mashanov, Y. J. Yang, H. H. Cheng, G. E. Chang, R. A. Soref and G. Sun, *Appl. Phys. Lett.*, 2013, **103**, 231907.
- 6 N. Huo and G. Konstantatos, *Adv. Mater.*, 2018, **30**, 1801164.
- 7 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666–669.
- 8 D. J. Late, B. Liu, H. S. S. R. Matte, V. P. Dravid and C. N. R. Rao, *ACS Nano*, 2012, **6**, 5635–5641.
- 9 D. J. Late, Y.-K. Huang, B. Liu, J. Acharya, S. N. Shirodkar, J. Luo, A. Yan, D. Charles, U. V. Waghmare, V. P. Dravid and C. N. R. Rao, *ACS Nano*, 2013, **7**, 4879–4891.
- 10 C. Lee, X. Wei, J. W. Kysar and J. Hone, *Science*, 2008, **321**, 385–388.
- 11 B. Chitara and A. Ya'akovovitz, *Nanoscale*, 2018, **10**, 13022–13027.
- 12 K. Liu, Q. Yan, M. Chen, W. Fan, Y. Sun, J. Suh, D. Fu, S. Lee, J. Zhou, S. Tongay, J. Ji, J. B. Neaton and J. Wu, *Nano Lett.*, 2014, **14**, 5097–5103.
- 13 T. J. Octon, V. K. Nagareddy, S. Russo, M. F. Craciun and C. D. Wright, *Adv. Opt. Mater.*, 2016, **4**, 1750–1754.
- 14 X. Chen, X. Lu, B. Deng, O. Sinai, Y. Shao, C. Li, S. Yuan, V. Tran, K. Watanabe, T. Taniguchi, D. Naveh, L. Yang and F. Xia, *Nat. Commun.*, 2017, **8**, 1–7.
- 15 X. Wang, W. Tian, M. Liao, Y. Bando and D. Golberg, *Chem. Soc. Rev.*, 2014, **43**, 1400–1422.
- 16 X. Yu, S. Zhang, H. Zeng and Q. J. Wang, *Nano Energy*, 2016, **25**, 34–41.
- 17 F. Luo, M. Zhu, Y. tan, H. Sun, W. Luo, G. Peng, Z. Zhu, X.-A. Zhang and S. Qin, *AIP Adv.*, 2018, **8**, 115106.
- 18 Q. Li, Q. Zhou, L. Shi, Q. Chen and J. Wang, *J. Mater. Chem. A*, 2019, **7**, 4291–4312.
- 19 L. Zhang, S. Shen, M. Li, L. Li, J. Zhang, L. Fan, F. Cheng, C. Li, M. Zhu, Z. Kang, J. Su, T. Zhai and Y. Gao, *Adv. Opt. Mater.*, 2019, **7**, 1801744.
- 20 T. Limbu, B. Chitara, J. D. Orlando, M. G. Cervantes, S. Kumari, Q. Li, Y. Tang and F. Yan, *J. Mater. Chem. C*, 2020, **8**, 4722–4731.

- 21 J. Wu, H. Yuan, M. Meng, C. Chen, Y. Sun, Z. Chen, W. Dang, C. Tan, Y. Liu, J. Yin, Y. Zhou, S. Huang, H. Q. Xu, Y. Cui, H. Y. Hwang, Z. Liu, Y. Chen, B. Yan and H. Peng, *Nat. Nanotechnol.*, 2017, **12**, 530–534.
- 22 J. Li, Z. Wang, Y. Wen, J. Chu, L. Yin, R. Cheng, L. Lei, P. He, C. Jiang, L. Feng and J. He, *Adv. Funct. Mater.*, 2018, **28**, 1706437.
- 23 Q. Wei, R. Li, C. Lin, A. Han, A. Nie, Y. Li, L.-J. Li, Y. Cheng and W. Huang, *ACS Nano*, 2019, **13**, 13439–13444.
- 24 H. Yang, W. Chen, X. Zheng, D. Yang, Y. Hu, X. Zhang, X. Ye, Y. Zhang, T. Jiang, G. Peng, X. Zhang, R. Zhang, C. Deng and S. Qin, *Nanoscale Res. Lett.*, 2019, **14**, 371.
- 25 C. Tan, M. Tang, J. Wu, Y. Liu, T. Li, Y. Liang, B. Deng, Z. Tan, T. Tu, Y. Zhang, C. Liu, J.-H. Chen, Y. Wang and H. Peng, *Nano Lett.*, 2019, **19**, 2148–2153.
- 26 J. Wu, C. Qiu, H. Fu, S. Chen, C. Zhang, Z. Dou, C. Tan, T. Tu, T. Li, Y. Zhang, Z. Zhang, L.-M. Peng, P. Gao, B. Yan and H. Peng, *Nano Lett.*, 2019, **19**, 197–202.
- 27 H. Yang, C. Tan, C. Deng, R. Zhang, X. Zheng, X. Zhang, Y. Hu, X. Guo, G. Wang, T. Jiang, Y. Zhang, G. Peng, H. Peng, X. Zhang and S. Qin, *Small*, **0**, 1904482.
- 28 J. Wu, Y. Liu, Z. Tan, C. Tan, J. Yin, T. Li, T. Tu and H. Peng, *Adv. Mater.*, 2017, **29**, 1704060.
- 29 J. Li, Z. Wang, J. Chu, Z. Cheng, P. He, J. Wang, L. Yin, R. Cheng, N. Li, Y. Wen and J. He, *Appl. Phys. Lett.*, 2019, **114**, 151104.
- 30 E. P. Painter, *Chem. Rev.*, 1941, **28**, 179–213.
- 31 X. Zhang, Y. Liu, G. Zhang, Y. Wang, H. Zhang and F. Huang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 4442–4448.
- 32 Z. Wu, H. Yu, S. Shi and Y. Li, *J. Mater. Chem. A*, 2019, **7**, 14776–14789.
- 33 A. L. Pacquette, H. Hagiwara, T. Ishihara and A. A. Gewirth, *J. Photochem. Photobiol. Chem.*, 2014, **277**, 27–36.
- 34 C. Huang, H. Yu, J. Chen, J. Zhang, Z. Wu and C. Hou, *Sol. Energy Mater. Sol. Cells*, 2019, **200**, 110030.
- 35 E. A. Bondarenko, E. A. Streltsov, M. V. Malashchonak, A. V. Mazanik, A. I. Kulak and E. V. Skorb, *Adv. Mater.*, 2017, **29**, 1702387.
- 36 E. A. Bondarenko, E. A. Streltsov, A. V. Mazanik and A. I. Kulak, *ChemElectroChem*, 2019, **6**, 2474–2481.
- 37 M. Wu and X. C. Zeng, *Nano Lett.*, 2017, **17**, 6309–6314.
- 38 K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2008, **41**, 653–658.
- 39 A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder and K. A. Persson, *APL Mater.*, 2013, **1**, 011002.
- 40 T. Ghosh, M. Samanta, A. Vasdev, K. Dolui, J. Ghatak, T. Das, G. Sheet and K. Biswas, *Nano Lett.*, 2019, **19**, 5703–5709.
- 41 T. Cheng, C. Tan, S. Zhang, T. Tu, H. Peng and Z. Liu, *J. Phys. Chem. C*, 2018, **122**, 19970–19980.
- 42 P. Hu, Z. Wen, L. Wang, P. Tan and K. Xiao, *ACS Nano*, 2012, **6**, 5988–5994.
- 43 Q. Fu, C. Zhu, X. Zhao, X. Wang, A. Chaturvedi, C. Zhu, X. Wang, Q. Zeng, J. Zhou, F. Liu, B. K. Tay, H. Zhang, S. J. Pennycook and Z. Liu, *Adv. Mater.*, 2019, **31**, 1804945.
- 44 P. Luo, F. Zhuge, F. Wang, L. Lian, K. Liu, J. Zhang and T. Zhai, *ACS Nano*, 2019, **13**, 9028–9037.
- 45 Chi On Chui, A. K. Okyay and K. C. Saraswat, *IEEE Photonics Technol. Lett.*, 2003, **15**, 1585–1587.
- 46 N. Youngblood, C. Chen, S. J. Koester and M. Li, *Nat. Photonics*, 2015, **9**, 247–252.
- 47 T.-F. Zhang, Z.-P. Li, J.-Z. Wang, W.-Y. Kong, G.-A. Wu, Y.-Z. Zheng, Y.-W. Zhao, E.-X. Yao, N.-X. Zhuang and L.-B. Luo, *Sci. Rep.*, 2016, **6**, 1–8.
- 48 T. Mueller, F. Xia and P. Avouris, *Nat. Photonics*, 2010, **4**, 297–301.

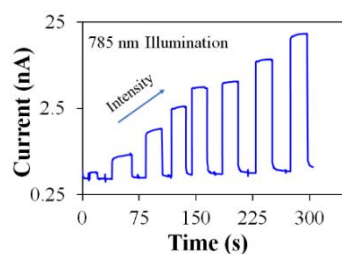
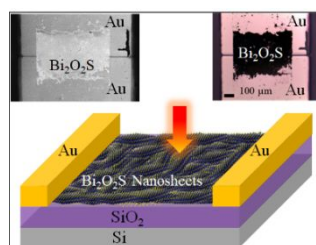
- 49 X. Wang, P. Wang, J. Wang, W. Hu, X. Zhou, N. Guo, H. Huang, S. Sun, H. Shen, T. Lin, M. Tang, L. Liao, A. Jiang, J. Sun, X. Meng, X. Chen, W. Lu and J. Chu, *Adv. Mater.*, 2015, **27**, 6575–6581.
- 50 F. Gong, F. Wu, M. Long, F. Chen, M. Su, Z. Yang and J. Shi, *Phys. Status Solidi RRL – Rapid Res. Lett.*, 2018, **12**, 1800310.
- 51 G. Chen, Y. Yu, K. Zheng, T. Ding, W. Wang, Y. Jiang and Q. Yang, *Small Weinh. Bergstr. Ger.*, 2015, **11**, 2848–2855.
- 52 F. Wang, L. Li, W. Huang, L. Li, B. Jin, H. Li and T. Zhai, *Adv. Funct. Mater.*, 2018, **28**, 1802707.
- 53 O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic and A. Kis, *Nat. Nanotechnol.*, 2013, **8**, 497–501.
- 54 F. P. García de Arquer, A. Armin, P. Meredith and E. H. Sargent, *Nat. Rev. Mater.*, 2017, **2**, 1–17.
- 55 R. Swartwout, M. T. Hoerantner and V. Bulović, *ENERGY Environ. Mater.*, 2019, **2**, 119–145.

ToC Entry

Keyword: Solution-processing, $\text{Bi}_2\text{O}_2\text{S}$, IR photodetectors

Basant Chitara, Tej B. Limbu, Jason D. Orlando, Yongan Tang, and Fei Yan*

Ultrathin $\text{Bi}_2\text{O}_2\text{S}$ Nanosheets Near-Infrared Photodetectors



Solution-processed $\text{Bi}_2\text{O}_2\text{S}$ nanosheets demonstrate high NIR photodetection with a photoresponsivity of 4 A/W, an external quantum efficiency of 630%, and a normalized photocurrent-to-dark-current ratio of 1.3×10^{10} per watt with a fast response time of 100 ms.