Single-crystalline In$_2$S$_3$ nanowire-based flexible visible-light photodetectors with an ultra-high photoresponse†

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With a band gap of 2.28 eV, In$_2$S$_3$ is an excellent candidate for visible-light sensitive photodetectors. By growing single-crystalline In$_2$S$_3$ nanowires via a simple CVD method, we report the fabrication of high-performance single-crystal In$_2$S$_3$ nanowire-based flexible photodetectors. The as-fabricated flexible photodetectors exhibited an ultra-high on/off ratio up to $10^6$ and a high sensitivity to visible incident light with responsivity and quantum efficiency as high as $7.35 \times 10^4$ A W$^{-1}$ and $2.28 \times 10^7\%$, respectively. Besides, the flexible photodetectors were demonstrated to possess a robust flexibility and excellent stability. With these favorable merits, In$_2$S$_3$ nanowires are believed to have a promising future in the application of high performance and flexible integrated optoelectronic devices.

Introduction

Photodetectors have always been a hot topic in both scientific and technical research fields, due to their special usage in many aspects of daily life and military/aerospace applications, such as optical fiber communication, flame sensing, disaster rescue, digital imaging and early rocket plume detection. With high sensitivity to specific spectrum bands, fast response speed and excellent stability, they are always the goals that researchers around the world are pursuing.

With a band gap of 2.0–2.3 eV and a defect spinel structure, the n-type $\beta$-In$_2$S$_3$ semiconductor is a potential candidate for high-performance visible photodetectors. Till now, various photodetectors based on $\beta$-In$_2$S$_3$ with different micro/nanostructures, such as thin films, nanoparticles, nanosheets, nanorods, etc., have been fabricated. Although photodetectors with $\beta$-In$_2$S$_3$ nanostructures exhibited an improved performance, the performance is still far from the actual needs. For example, In$_2$S$_3$ nanoparticle- and nanosheet-based devices showed responsivity less than 50 A W$^{-1}$ and a slow response speed of about 0.1 s, even after a doping with Cu$. One-dimensional nanostructures are believed to be better candidates for high performance photodetectors than nanoparticles due to their large surface-to-volume ratios and rationally designed surfaces. Unfortunately, the reported In$_2$S$_3$/Ag core/shell nanorod array gave almost the same performance as nanoparticles (low on/off ratio as 0.25, low responsivity as 40.05 A W$^{-1}$, and slow response time as 0.15 s). The results were believed to have a strong relationship with the less efficient nanostructure and poor crystal quality. Thus, it is still highly desirable to develop high performance photodetectors based on $\beta$-In$_2$S$_3$ nanowires either by improving the quality of the nanowire itself or by designing new structural devices.

Herein, we directly fabricated flexible visible-light photodetectors with high-quality single-crystalline $\beta$-In$_2$S$_3$ nanowires (NWs). The as-fabricated photodetectors exhibited an ultra-high on/off ratio up to $10^6$ and high sensitivity to visible incident light with responsivity and quantum efficiency as high as $7.35 \times 10^4$ A W$^{-1}$ and $2.28 \times 10^7\%$, respectively. All the parameters are several orders of magnitude higher than previously reported data on In$_2$S$_3$ devices. Besides, these flexible photodetectors, fabricated for the first time, possess robust flexibility and excellent stability, making it possible for them to be used for the next generation of flexible electronics.

Experiments

Material preparation and characterization

The syntheses of In$_2$S$_3$ NWs were carried out in a horizontal quartz tube furnace system via a facile chemical vapor deposition (CVD) method. In a typical process, In$_2$S$_3$ powder (Alfa Aesar, purity 99.995%) was first loaded in a ceramic boat serving as the source material and then sent to the center of a...
quartz tube. Before heating, the furnace was pumped to exclude the remaining air. Then the center of the quartz tube was heated to 900 °C at a rate of 30 °C min⁻¹ and kept for 2 h under a constant Ar (purity 99.999%) flow of 100 sccm. A pre-cleaned commercial n-type silicon wafer coated with a thin layer of gold nanoparticles was placed downstream, away from the center of the quartz tube by about 12–15 cm, to be used as the receiving substrate. After the reaction, the furnace was cooled to room temperature and a layer of dark-grayish red NW film product was found deposited on the substrate. The as-prepared product was characterized by X-ray diffraction (XRD; X’pert Pro, PANalytical B.V., Netherlands), field emission scanning electron microscopy (FE-SEM, Sirion 200) equipped with an energy-dispersive X-ray spectrometer (EDS), transmission electron microscopy (TEM; Philips CM 20) and room-temperature photoluminescence (PL) (Horiba JY HR800) with an excitation laser (Kimmon He-Cd laser) of 325 nm.

Fabrication of FET and photodetectors

To fabricate single-nanowire devices, the In₂S₃ nanowires were sonicated in ethanol and then deposited onto a rigid Si substrate covered with a 300 nm SiO₂ layer. A standard photolithography technique was carried out, followed by the Au/Ni (85 nm/15 nm) source and drain electrode deposition on two terminals of a single In₂S₃ nanowire. The flexible photodetectors were fabricated by similar processes on a PET substrate.

Devices measurements

Electronic and optoelectronic measurements of the fabricated devices were carried out with the four probe stations connected with a semiconductor characterization system (Keithley 4200-SCS). The illumination source for the photoresponse measurements was a power-adjustable monochromatic light source. All the measurements were performed in air and at room temperature.

Results and discussion

Fig. 1a shows the scanning electron microscopy (SEM) image of the as-synthesized In₂S₃ NWs. Nanowires were found to successfully synthesize under the conditions described. The crystal structure of the obtained NWs was confirmed by X-ray diffraction (XRD) and the corresponding XRD pattern is shown in Fig. S1.† As is shown, all the diffraction peaks in this pattern can be properly indexed to cubic β-In₂S₃, in good agreement with the standard data file (JCPDS no. 32-456). Fig. 1b displays the corresponding crystal structure of a cubic β-In₂S₃ unit cell which has a side length of 10.734 Å and shows that each In³⁺ connects with three S²⁻. The photoluminescence (PL) properties of the as-synthesized In₂S₃ NWs were studied at room temperature with a laser of ~70 μW cm⁻² and the corresponding spectrum is depicted in Fig. 1c. A strong exciton emission at 545 nm was observed in the test range from 330 nm to 800 nm. The band gap of the as-synthesized In₂S₃ NWs is thus calculated to be ~ 2.28 eV, in accordance with previous reports.

To get information about the microstructures, the synthesized In₂S₃ NWs were studied by transmission electron microscopy (TEM). As depicted in Fig. 1d, a typical NW appears relatively homogeneous without any significant domain boundaries, indicating a possible single-crystalline nature. Its high-resolution TEM (HRTEM) image is shown in Fig. 1e. The clearly resolved interplanar spacing was measured to be 0.38 nm, corresponding to the (220) planar spacing of cubic β-In₂S₃. The corresponding selected area electron diffraction (SAED) pattern (top right corner inset, Fig. 1e) further confirms the single-crystalline nature of the as-synthesized NWs. The energy-dispersive X-ray spectrometry (EDS) was performed to exhibit the distribution of the indium and sulfur element along the NW body, shown in Fig. 1f–h. The homogeneous spacing distribution suggests a uniform chemical composition along the NW axial direction.
It is generally believed that In$_2$S$_3$ is a typical n-type semiconductor through the sulfur deficiency in the crystal. To get information on the electronic transport properties of the synthesized In$_2$S$_3$ NWs, we fabricated single NW back-gate field-effect transistors (FETs) using a conventional photolithographic and lift-off technique. Fig. S2† presents a schematic diagram of the In$_2$S$_3$ NW FET, which was fabricated on a 300 nm SiO$_2$-coated Si substrate. The corresponding SEM image of the device is shown in the inset, where the channel width of 9 μm and the NW length between two electrodes of 9.72 μm, can be clearly seen. To form a good contact, a Au/Ni (85 nm/15 nm) bilayer was deposited by electron-beam evaporation as the electrodes. Fig. S3a and 3b† show the drain current versus drain voltage and the drain current versus gate voltage curves of the device measured. The drain current was found to increase with gate voltage, indicating the typical n-type semiconductor behavior of our In$_2$S$_3$ NWs.

Flexible electronics have drawn extensive attention because of their attractive properties such as flexibility, light weight, shock resistance, etc. Significant advancements have been achieved and many kinds of flexible devices have been fabricated, such as flexible transistors, photodetectors, energy storage and conversion devices, artificial skins, and organic light-emitting diode displays. In this work, we directly fabricated flexible photodetectors using the as-synthesized In$_2$S$_3$ NWs to investigate their photoconductive properties. Fig. 2a shows a three-dimensional (3D) simulated schematic diagram of the as-fabricated single In$_2$S$_3$ NW flexible photodetectors. An SEM image of the corresponding device is demonstrated in Fig. 2b. Au/Ni electrodes (85 nm/15 nm) with a pattern of distance 9 μm were made using conventional photolithography and lift-off process. The NW length between the two electrodes was 9.6 μm and the NW had a diameter of about 359.4 nm. Fig. S4† is the current versus voltage (I–V) curve of the flexible device in the dark. The current of the In$_2$S$_3$ NW was about 0.12 pA at a voltage of 5 V. Photocurrent versus voltage (I–V) plots measured under illumination with lights of different wavelength are given in Fig. 2c. The photocurrent of the device was found to increase sharply under illumination and could approach 293 nA under 450 nm light at a density of 176.7 μW cm$^{-2}$. The corresponding photocurrent versus dark current ($I_{	ext{photo}}/I_{	ext{dark}}$) was ~10$^6$, six orders of magnitude higher than the best $I_{	ext{photo}}/I_{	ext{dark}}$ values reported till now. All the photocurrents $versus$ voltage curves under different wavelengths (300 nm to 600 nm) reveal strong and obvious photon-induced current phenomena, suggesting an excellent photosresponse ability of the device in the visible spectrum.

In order to get an intuitive result of the spectral response for our In$_2$S$_3$ NW-based device, Fig. 2d shows the computed spectral responsivity ($R_s$) and external quantum efficiency (EQE) results from Fig. 2c. $R_s$ and EQE are known as key parameters used to evaluate the properties of a photodetector, and they can be expressed by the following equations:

$$ R_s = \frac{\Delta I}{P} $$

$$ \text{EQE} = \frac{I_{\text{light}}}{I_{\text{dark}}} R_s = \frac{h\nu}{e\lambda} $$

where $P$ is the incident light power, $S$ is the effective illuminated area, $h$ is Planck’s constant, $c$ is the velocity of light, $e$ is the electronic charge and $\lambda$ is the light wavelength. From the calculated results, at a bias of 5 V, the flexible photodetectors get a peak $R_s$ value of 7.35 × 10$^4$ A W$^{-1}$ and an EQE of 2.28 × 10$^{-7}\%$ at 400 nm. Both values are several orders of magnitude higher than the reported data on In$_2$S$_3$ nanostructures. In addition, the same spectral responsivity trend can be seen at different bias voltages (Fig. 2d). The different responsivities under different wavelengths are due to different spectral absorptions, which is in good agreement with previous reports.

Specific detectivity ($D^*$) is also an important parameter reflecting the sensitivity of a photodetector to incident light and it can be expressed by the equations:

$$ D^* = \frac{(BS)^{1/2}}{\text{NEP}} \quad \text{(cm Hz}^{1/2} \text{W}^{-1}) $$

$$ \text{NEP} = \frac{I_{\text{noise}}}{R_s} \quad \text{(W)} $$

where $B$ is band width, $S$ is the effective area of the detector, NEP is the noise equivalent power, $I_{\text{noise}}$ is the measured noise current and $R_s$ is the responsivity. In the case of a low noise from the dark current being the major contributor to the noise limit of the detectivity, the detectivity can be simplified as:

$$ D^* = \frac{R_s}{(2eI_{\text{dark}}/S)^{1/2}} $$

Calculated from the above equations, our flexible In$_2$S$_3$ NW photodetector achieved a high $D^*$ value up to 2.4 × 10$^{14}$ Jones under 400 nm light at a 5 V bias.
For semiconducting nanowires, a large surface-to-volume ratio generally leads to the existence of abundant oxygen-related hole-trap states at the NW surface, which has a significant impact on the charge carrier transport and photoconduction properties of the NW-based photodetectors. As a typical n-type semiconductor, the surface of the In$_2$S$_3$ NWs has a high density of surface-bound states for electrons. At normal atmospheric pressure, oxygen molecules are easily combined with the free electrons on the In$_2$S$_3$ NW surface via $\text{O}_2 + e^- \rightarrow \text{O}^{-2}$. This process leads to a depletion layer near the NW surface, resulting in increased carrier densities. Under illumination, large amounts of electron-holes are generated rapidly. The photogenerated holes move to the NW surface under the electric field in a radial direction and recombine with the absorbed oxygen molecules via $\text{h}^+ + \text{O}^{-2} \rightarrow \text{O}_2$, which in turn releases back the captured free electrons, leading to a further increase of the free electron concentration. Due to the existence of an internal electric field, the recombination of holes and free electrons will be slowed down and the life time of the photocarrier ($t_{\text{life}}$) is thus prolonged. Eventually, we get a high EQE value for the In$_2$S$_3$ NW photodetector.

Our single $\beta$-In$_2$S$_3$ NW flexible photodetectors are demonstrated to have an excellent intensity response in Fig. 3a, which shows the $I$–$V$ curves of the device in the dark and under a 450 nm light nm illumination with various intensities. Apparently, the $I$–$V$ curves also exhibit a good linear relationship and the photocurrent increases with increasing light intensity at an identical voltage. The photoresponse of the device in the dark and under different light irradiance levels was also measured with a 450 nm light of light intensity ranging from 0 to 524 $\mu$W cm$^{-2}$ at a constant bias of 5 V. As is shown in Fig. 3b, the device was first tested in the dark and the corresponding current was nearly negligible. While the light intensity switched to a higher level, the current rapidly increased to another stable value, highly consistent with the $I$–$V$ changes in Fig. 3a.

**Fig. 3.** (a) $I$–$V$ and (b) $I$–$T$ curves of the device in the dark as well as under illumination with a 450 nm light of different intensities. (c) Photocurrent versus light intensity plot at a bias of 5 V, with $I = 9.366 \times P^{0.672}$. (d) Photocurrent versus time plots of the single NW photodetector under illumination with a 450 nm light at a bias of 2 V, 4 V and 8 V; the light intensity was kept constant at 177 $\mu$W cm$^{-2}$. (e) A transient response by illuminating with a 450 nm light pulse chopped at a frequency of 20 Hz with the reference signal. (f) An enlarged portion of the photocurrent showing the changes in detail.
Fig. 3c shows the dependence of photocurrent on light intensity curves measured at a constant voltage of 5 V. The dependence relation is often expressed by a power law, $\Delta I = aP^\theta$, where $\Delta I = I_{\text{photo}} - I_{\text{dark}}$, $a$ is a proportionality constant, $P$ is the light intensity and $\theta$ is an empirical value.\textsuperscript{30} After the fitting calculation we get a power law as $\Delta I = 9.366 \times P^{0.672}$, which not only suggests a strong dependence relationship between the photocurrent and light intensity but also indicates multiple trap states according to previous reports.\textsuperscript{29}

The time-related photoresponse of the flexible photodetector is shown in Fig. 3d, and is measured by turning a 450 nm light on and off with a period of 10 seconds. As is shown, under a fixed optical power of 177 $\mu$W cm$^{-2}$ and at different bias voltages of 2 V, 4 V and 8 V, the photodetector exhibits highly stable and reproducible properties in all three cases. To give a relatively accurate estimation of the photoresponse time, the devices were tested with a 450 nm light pulse chopped at a frequency of 20 Hz with the reference signal. As is shown in

<table>
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<th>Photodetectors</th>
<th>Response time</th>
<th>$I_{\text{on}}/I_{\text{off}}$</th>
<th>Responsivity (A W$^{-1}$)</th>
<th>EQE (%)</th>
<th>Reference</th>
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<td>40.05</td>
<td>9313</td>
<td>18</td>
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<tr>
<td>In$_2$S$_3$ nanowires</td>
<td>6.5 ms/9.5 ms</td>
<td>$2.4 \times 10^6$</td>
<td>$7.35 \times 10^4$</td>
<td>2.28 $\times 10^7$</td>
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![Fig. 4](image-url)

**Fig. 4** (a–e) Digital photographs of the device under five different bending states (0°, 120°, 90°, 60°, 30°). (f) $I$–$V$ curves of the flexible device obtained at different bend angles under a 450 nm light with an intensity of 177 $\mu$W cm$^{-2}$; (a–e) represent the corresponding states in a–e respectively. (g) Photocurrent stability test according to different bending angles. (h) Typical $I$–$T$ curve recorded continuously over 700 s at a 450 nm incident power light with an intensity of 524 $\mu$W cm$^{-2}$. (i) $I$–$V$ curves of the flexible device without bending and after 50, 150 and 200 cycles of bending, respectively.
Fig. 3e and 3f, the rise time and decay time of our In$_2$S$_3$ NW devices are only 6.5 ms and 9.5 ms, respectively. Both the response and decay times are much shorter than many other NW-based photodetectors.$^{31-34}$

Based on the above results, we can see that our In$_2$S$_3$ NW based flexible photodetectors exhibited a much better performance than all the previously reported In$_2$S$_3$ nanostructure devices, such as nanosheets, nanoparticles, and core–shell nanowires. Table 1 lists the comparison of the critical parameters between this work and the previous reports on intrinsic and doping In$_2$S$_3$ nanostructures. The excellent properties of our device can be ascribed to the following reasons. First, the 1-D NW structure has a large surface-to-volume ratio which tends to induce defects and dangling bonds on the surface of the NW, as mentioned before. This will increase the recombination rate of carriers and shorten the decay time, and thus enhance the photoresponse of NWs. Second, the intrinsic n-type behavior of In$_2$S$_3$ is due to the sulfur deficiency, meaning abundant deep trap states exist in In$_2$S$_3$ NWs. According to previous reports, this can prolong the photocarrier lifetime, resulting in an enhanced $R_0$ and EQE.$^{35}$ Third, the metal contact with the NW also proved to have an effect on the photoresponse. A good ohmic contact, proper NW radii and short electrode distance will all contribute to the short transit time ($t_{\text{trans}}$), thus leading to an enhanced response time and responsivity.$^{13,36}$

For a promising flexible photodetector, the flexibility and stability are highly valued factors for practical applications. In order to investigate the flexibility and stability of our flexible In$_2$S$_3$ NW-based photodetector, $I$–$V$ tests under different bending angles were carried out to give a relatively precise assessment. Fig. 4a–e show the device under five different bending conditions, from Fig. 4a–4e, with the bending angles of 0°, 120°, 90°, 60° and 30°, respectively. Fig. 4f shows the corresponding $I$–$V$ curves with a 450 nm incident light illumination of 177 μW cm$^{-2}$. It can be easily found that the photocurrent under different bending states obtained almost the same gain as the non-bending angle state (0°). It should be mentioned that the $I$–$V$ curves after bending did not show as good an ohmic contact as the non-bending case, which is reasonable and understandable since, under a bending state, the gap distance will be changed and further affect the resistance.$^{37}$ In addition, bending may also affect the contact between NW and metal electrodes. Even so, the photocurrents maintained at about 293 ± 19 nA and the on/off ratio stayed at a high level of about ~2.4 × 10$^6$. Meanwhile, the relative change of the current at different biases with respect to the non-bending $I$–$V$ curve is shown in Fig. 4g. Changes are totally acceptable, confirming the robustness of the flexible device.

Excellent flexible photodetectors should not only have the features of a stable performance under different bending conditions, but also should stay reliable for long-term application. Fig. 4h shows a typical $I$–$T$ curve under a 450 nm light with a relatively high intensity of 524 μW cm$^{-2}$ and at a high bias of 5 V. This clearly shows that, while the $I$–$T$ curve recorded continuously for nearly 700 s, the photocurrent stayed almost the same without an obvious decline. On the other hand, $I$–$V$ curves of the flexible device after bending for different cycles are shown in Fig. 4i. The red curve is the $I$–$V$ test without bending; others are the results after bending 50, 100, 150 and 200 times, respectively. One bending cycle is defined as being bent from state two in Fig. 4b to state five in Fig. 4e and then returned to state one in Fig. 4a. From Fig. 4i, it can be easily seen that the photocurrent was hardly affected, even after being bent for 200 cycles. All the measurements have demonstrated that our In$_2$S$_3$ NW-based flexible photodetectors have an excellent performance and are promising for future flexible and portable device applications.

Conclusions

In summary, high-quality single-crystalline cubic β-In$_2$S$_3$ NWs were synthesized via a facile CVD method using In$_2$S$_3$ powder as the material source. Single NW field-effect transistors confirmed the n-type semiconducting behavior of the as-grown NWs. More importantly, single In$_2$S$_3$ NW photodetectors on a flexible PET substrate exhibited excellent spectral responsivity (7.35 × 10^4 A W$^{-1}$) in the visible spectrum, an extremely high EQE value (2.28 × 10^7%) and a high $D^*$ (2.4 × 10$^{14}$ Jones), a very high $I_{\text{on}}/I_{\text{off}}$ (~10^6) and a fast response speed (~10 ms). Excellent mechanical flexibility and good stability of the devices with a robust performance over a long time ensure their possible application in nanoscale photodetectors and optoelectronic circuits, especially in future flexible, portable and wearable electronics.

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Notes and references