HfX₃(X=Se and S)/graphene composites for flexible photodetectors from visible to near-infrared

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ABSTRACT Flexible photodetectors from 405 to 980 nm based on HfSe₃ or HfS₃ nanobelts (NBs)/graphene composites were fabricated on polypropylene (PP) films. Compared with HfSe₃ or HfS₃ NB photodetectors, the flexible composite photodetector showed enhancement of photoresponsivity. For substance, under the illumination light of 405 nm (14.4 mW/cm²), the responsivities of HfSe₃ NBs, HfSe₃ NBs/GO (graphene oxide) and HfSe₃ NBs/RGO (reduced graphene oxide) photodetectors were 1.1×10^{-4} , 4.3×10^{-3} and 0.5 (mA/W), respectively, while those of HfS₃ NBs, HfS₃ NBs/GO and HfS₃ NBs/RGO photodetectors were 0.11, 0.92 and

0.55 (mA/W), respectively. Meanwhile, these photodetectors exhibited excellent durability and stability after they were placed for 3 months and bended 500 times. So the composites are promising optoelectronic materials, and the flexible photodetectors are high-performance photodetectors from visible to near-infrared.

KEYWORDS: Chalcogenides, Nanostructures, Composites, Optical properties, X-ray diffraction

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1. Introduction

In the last decade, photodetectors based on one-dimensional (1D) nanostructures have been reported such as ZnS nanowires, ZnO nanorods, WO₃ nanowires, TiO₂ nanotubes, In₂Ge₂O₇ nanowires, Zn₂GeO₄ nanowires, Ge nanowires, In₂Se₃ nanowires, CdSe nanowires, Zn₃P₂ nanowires, InP nanowires, ZrS₃ nanobelts, and so on [1–13]. 1D nanostructures have been applied in photodetectors because of their large ratio of length- to- diameter which facilitates electron transport compared to the quantum dots. Recently, our group has reported ultraviolet-visible (UV-vis) photodetectors based on HfSe₃ and HfS₃ nanobelts (NBs) [14–16]. To improve responsivity of the photodetectors, we expect to find a material which can be compounded with HfSe₃ or HfS₃ NBs.

Graphene is a two-dimensional (2D) material with a high electrical conductivity and optical transparency in whole range of light waves [17, 18], so it can be fabricated as nanoelectronic and optoelectronic devices [19–21]. For example, photodetector

based on single graphene showed near-infrared (NIR) photoresponse [22]. Graphene/Ga₂O₃/SiC heterojunction displayed enhancement of UV photoresponse [23]. Monolayer graphene/ZnO nanorod heterojunction revealed high-performance UV detection [24]. Because graphenes have two types of graphene oxide (GO) and reduced graphene oxide (RGO), and both have different performance, here a few flexible photodetectors based on HfSe₃/GO (GRO) and HfS₃/GO (GRO) composites were fabricated on polypropylene (PP) film. Compared with HfS₃ and HfSe₃ nanobelt photodetectors, the flexible photodetectors of the composites showed an enhancement of photoresponsivity.

2. Experimental procedures

2. 1. Synthesis of HfSe₃ and HfS₃ nanobelts

HfSe₃ and HfS₃ nanobelts were synthesized by chemical vapor transport [14, 16]. In a typical procedure, selenium powders (99.99%, 132.7 mg) or sulfur powders (99.5%, 53.8 mg) were mixed with hafnium powders (99.5%, 100 mg), respectively, and sealed in two quartz tubes (ϕ 6 mm $\times$ 12 cm) under vacuum (10^{-2} Pa), respectively, and then the two quartz tubes were placed at the middle of two conventional horizontal furnaces (temperature gradient: 10 Kcm⁻¹), and heated at 650 °C for 24 h and 6 h, respectively. Subsequently, the furnaces were naturally cooled down to room temperature. The black (HfSe₃) and yellow (HfS₃) nanobelts were extracted from the sealed quartz tubes, respectively. X-ray diffraction (XRD) patterns of HfSe₃ and HfS₃ nanobelts were shown in Fig. S1 (a) and (b), which were well coincided with HfSe₃ (JCPDS No. 29-0654) and HfS₃ (JCPDS No. 29-0655), respectively (Supplementary

Fig. S1). RGO and GO were prepared according to modified Hummer method [25].

2. 2. Preparation of HfSe_3/GO (RGO) and HfS_3/GO (RGO) composites

First, 0.5 mL GO suspension (6 mg/mL) and 7 mL ethanol were mixed and sonicated in ultrasonic cleaner for 30 minutes, while 2 mg RGO and 2 mL ethanol were mixed and sonicated under the same condition. Then, 0.02 g HfSe_3 powders were mixed with 1 mL as-dispersed GO and 0.4 mL as-dispersed RGO, respectively, and sonicated for 10 minutes to form HfSe_3/GO and HfSe_3/RGO composites. Finally, weight ratio of HfSe_3 and GO (or RGO) is 50:1. Same, HfS_3/GO and HfS_3/RGO composites were prepared.

2. 3. Fabrication of the flexible photodetectors

The flexible photodetectors were fabricated on PP film as shown in Fig. 1a. First, double-side adhesive tape was adhered to flexible PP film, and then material dispersions such as HfSe_3 (or HfS_3) nanobelts or the above composites suspension, were dripped dropwise onto the PP film, dried naturally at room temperature. Subsequently, a rectangular gridding mask was covered on the top of the film. Ti/Au (10 nm/50 nm) film was evaporated on the film by High Vacuum Turbo Evaporator, and then the mask was carefully peeled off. Finally, the flexible photodetectors were obtained. Fig. 1b demonstrated an optical micrograph of the flexible HfSe_3 -based photodetector, and the gap between two electrodes is about 121.03 μm which is almost the same in other photodetectors. Inset exhibited the photograph of the flexible photodetector.

2. 4. Characterization and measurements

The products were characterized by a Shimadzu XRD-6000 X-ray diffraction with graphite monochromatized Cu K $_{\alpha 1}$ radiation (XRD), a Hitachi S-4800 field-emission scanning electron microscope (SEM) with energy-dispersive X-ray spectrometer (EDX), and a Shimadzu UV-3600 spectrophotometer. The current-voltage (I - V) and the current-time (I - t) characteristics of the photodetectors were recorded by SM-4 Probe Station and Keithley 236 source meter. Optical power was measured with FZ-A radiometer (made in China).

3. Results and discussion

Fig. 2a exhibits a scanning electron microscopy (SEM) image of as-synthesized HfSe $_3$ nanobelts. The length ranges from 520 nm to several micrometers, and the width is about 30 to 350 nm. Fig. 2b and c show the SEM images of HfSe $_3$ /GO and HfSe $_3$ /RGO, respectively, which can be clearly seen that HfSe $_3$ nanobelts were wrapped with graphene. Fig. 2d reveals the SEM image of HfS $_3$ nanobelts with the width of 50–600 nm and length from several to tens of micrometers. Fig. 2e and f showed the SEM images of HfS $_3$ /GO and HfS $_3$ /RGO composites, respectively. Same, HfS $_3$ nanobelts were also wrapped with GO (RGO). Fig. 3a shows the UV-vis absorption spectra of HfSe $_3$ NBs, HfSe $_3$ /GO, and HfSe $_3$ /RGO dispersions. HfSe $_3$ NBs dispersions show an absorption band from 300 to 840 nm, and there are the characteristic absorption peaks at 428, 636, and 814 nm. HfSe $_3$ /GO dispersions reveal a stronger absorption band from 250 to 980 nm, and there are the characteristic absorption peaks at 426, 619, and 810 nm. HfSe $_3$ /RGO dispersions display the strongest absorption band from 250 to 850 nm, and there are the characteristic

absorption peaks at 426, 618, and 810 nm. It shows that the characteristic absorptions come from HfSe₃, and the absorptions enhance as GO and RGO are added, which is beneficial to enhancement of photosensitivity. The UV-vis absorption spectra of HfS₃ NBs, HfS₃/GO, and HfS₃/RGO dispersions are showed in Fig. 3b, which reveals the dispersions have good absorption from 250 to 1000 nm. Same, the absorptions enhance as GO and RGO are added.

To investigate the effects of graphene on photosensitivity, the photodetectors based on HfSe₃ NBs, HfSe₃/GO composites, and HfSe₃/RGO composites were tested under dark condition and monochromatic light with different wavelengths. Fig. 4a shows the $I-V$ curves of HfSe₃-nanobelt photodetector under dark and light illumination. They reveal good photoresponse from 405 nm to 980 nm, and the photocurrent at 405 nm is the highest. The linear $I-V$ curves demonstrate the ohm contact between the nanobelts and the electrode. The responsivity ($R_\lambda = \Delta I/(PS)$) and external quantum efficiency ($EQE = hcR_\lambda/(e\lambda)$) are two significant parameters to decide photoelectric properties [26, 27]. Where ΔI is the difference between photo-illuminating current and dark current, P is the light power density irradiated on the device, S is the effective irradiated area, h is the Planck's constant, c is the velocity of light, e is the electronic charge, and λ is the light wavelength. The transient photoresponse ($I-t$) curve of the HfSe₃ photodetector is shown in Fig. 4b under illumination of 405-nm light of 14.4 mW/cm² and dark with a photoswitching period of 1 s at a bias voltage of 5 V. According to the above formulas, the R_λ and EQE are 1.1×10^{-4} mA/W and $3.32 \times 10^{-5}\%$, respectively. The rise /decay time is about 0.82 s

/0.57 s, and the on-off ratio of current ($I_{\text{on/off}}$) is 1.22. The time interval for current to increase from 10% to 90% of the peak value is defined as the rise time, conversely as the decay time [28]. Fig. 4c shows the $I-t$ curve of the HfSe_3 photodetector under illumination of 980-nm light with the optical power of 34.4 mW/cm^2 , here the R_d , EQE, the rise/decay time and $I_{\text{on/off}}$ are $1.25 \times 10^{-6} \text{ mA/W}$, $1.58 \times 10^{-7} \%$, 0.66/0.4s and 1.03, respectively. Fig. 4d shows the $I-V$ curves of the HfSe_3/GO photodetector under illumination of different light, revealing good photoresponses from 405 to 980 nm, too. Figs. 4e and f show the $I-t$ curves of the HfSe_3/GO photodetector under illumination of 405-nm light with an optical power of 14.4 mW/cm^2 , and 980-nm light with an optical power of 34.4 mW/cm^2 at a bias of 5 V with a photoswitching period of 1 s, respectively. Fig. 4g shows the $I-V$ curves of HfSe_3/RGO composite photodetector under illumination of different light. It also shows good photoresponses from 405 to 980 nm. Figs. 4h and i display the $I-t$ curves of the HfSe_3/RGO photodetector under illumination of 405-nm light of 14.4 mW/cm^2 , and 980-nm light of 34.4 mW/cm^2 at a bias of 5 V with a photoswitching period of 1 s, respectively. The results under illumination of 405 nm and 980 nm are included in table 1 and 2, respectively. Based on the $I-t$ curves, the photodetectors under illumination of 405 and 980 nm light show good response. Under illumination of 405-nm light, the dark currents of the HfSe_3 , HfSe_3/GO and HfSe_3/RGO photodetectors are about 18 pA, 12.6 nA, and 275 nA, respectively, while the light currents are 3.9 pA, 0.2 nA, and 17 nA, respectively, so the dark and photo currents increase gradually, so that the photoresponses of HfSe_3 , HfSe_3/GO and HfSe_3/RGO photodetectors increase in turn.

The increase of the dark currents can be attributed to the increase of the conductivity of the materials, because the conductivity of RGO is higher than GO. The increase of the photocurrents may originate from heterostructure effect of HfSe₃ and GO (or RGO). Here all the photoresponses for 405nm are comparable with GaS nanobelt photodetector (490 nm, 0.23 mA/W [27]) except HfSe₃ and HfSe₃/GO photodetectors whereas all the photoresponses for 980 nm are greater than photodetector of SnS₂ nanosheet microsphere film (850 nm, 1.22×10^{-5} mA/W [29]) except HfSe₃ photodetector. So most of these devices have good photoresponses.

In order to study the influence of GO and RGO on HfS₃ photodetectors, flexible HfS₃ nanobelts/GO (or RGO) photodetectors are investigated by the same way. Fig. 5a exhibits the $I-V$ curves of HfS₃ nanobelts photodetector under dark condition and illumination, revealing good photoresponse from 405 to 980 nm. The $I-t$ curve of the device under 405-nm light illumination at a bias voltage of 5 V with a photoswitch period of 1 s is shown in Fig. 5b, displaying excellent photosensitive stability. Fig. 5c illustrates the $I-t$ curve of the HfS₃ photodetector under illumination of 980-nm light with an optical power of 34.4 mW/cm² at a bias voltage of 5 V with a photoswitch period of 1 s. Fig. 5d demonstrates the $I-V$ curves of HfS₃/GO photodetector. Figs. 5e and f show the transient responses of HfS₃/GO photodetector under 405-nm and 980-nm light illumination at a bias voltage of 5 V with a photoswitch period of 1 s, respectively. Fig. 5g exhibits the $I-V$ curves of HfS₃ NBs/RGO photodetector under light illumination from 405 nm to 980 nm. Figs. 5h and i show the transient responses of HfS₃/RGO photodetector under 405-nm and 980-nm light illumination at a bias of

5 V with a photoswitch period of 1 s, respectively. Based on the $I-t$ curves, the photodetectors also show good responses. Under illumination of 405-nm light, the dark currents of the HfS_3 , HfS_3/GO and HfS_3/RGO photodetectors are about 0.24 nA, 250 nA, and 450 nA, respectively, while the light currents are 3.4 nA, 36 nA, and 20 nA, respectively, so the dark currents increase gradually, and the photocurrents of the composites are higher than those of HfS_3 , so that the photoresponses of the composite photodetectors increase. The increase of the dark current can be attributed to that of the composite conductivity. In addition, photodetectors with GO under illumination of 980-nm light are stabler than those with RGO by $I-t$ curves. The results are also summarized in Table 1 and 2, respectively.

To investigate durability and stability of the photodetectors, the six photodetectors were tested after placed in air for 3 months and bended 500 times. Fig. 6(a–c) show the $I-t$ curves of HfSe_3 nanobelts, HfSe_3/GO composites and HfSe_3/RGO composites photodetectors under 405-nm light illumination with 14.4 mW/cm^2 at a bias voltage of 5 V with a photoswitching period of 1 s, which demonstrates these photodetectors still have a high photosensitivity and stability after placed in air for 3 months and bended 500 times. Fig. 6d–f displays the $I-t$ curves of HfS_3 nanobelts, HfS_3/GO composites, and HfS_3/RGO composites photodetectors under the same conditions, revealing that these photodetectors still have a high photosensitivity and stability after placed in air for 3 months and bended 500 times.

4. Conclusions

Flexible photodetectors based on HfSe_3/GO , HfSe_3/RGO , HfS_3/GO and HfS_3/RGO composites were fabricated for the first time. These photodetectors demonstrate a fast photoresponse and high sensitivity at visible to near-infrared lights. It is attributed that conductivity of the materials increases when GO or RGO is added. After placed for 3 months and bended 500 times, these photodetectors still show a good photosensitivity and fast response, indicating the durability and stability of these devices. Therefore, these photodetectors are decent photodetectors.

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Figure captions

Fig. 1. (a) Schematic illustration of the flexible nanobelts/graphene photodetector fabrication based on PP substrate. (b) Optical micrograph of the gap between two electrodes of flexible HfSe₃-based photodetector. Inset is its optical image.

Fig. 2. SEM images. (a) HfSe₃ nanobelts, (b) HfSe₃/GO composites, (c) HfSe₃/RGO composites, (d) HfS₃ nanobelts, (e) HfS₃/GO composites, and (f) HfS₃/RGO composites.

Fig. 3. UV-vis absorption spectra. (a) HfSe₃ nanobelts, HfSe₃/GO, and HfSe₃/RGO. (b) HfS₃ nanobelts, HfS₃/GO, and HfS₃/RGO.

Fig. 4. (a) I - V curves of HfSe₃ nanobelts photodetector under dark and illumination with the wavelength range from 405 nm to 980 nm. (b, c) I - t curves of HfSe₃ nanobelts under 405-nm and 980-nm light with an on-off period of 1 s at a bias voltage of 5 V, respectively. (d) I - V curves of HfSe₃/GO under dark and illumination with the wavelength range from 405 nm to 980 nm. (e, f) I - t curves of HfSe₃/GO under 405-nm and 980-nm light with an on-off period of 1 s at a bias voltage of 5 V, respectively. (g) I - V curves of HfSe₃/RGO under dark and illumination with the wavelength range from 405 nm to 980 nm. (h, i) I - t curves of HfSe₃/RGO under 405-nm and 980-nm light with an on-off period of 1 s at a bias voltage of 5 V, respectively.

Fig. 5. (a) I - V curves of HfS₃ nanobelts photodetector under dark and illumination with the wavelength range from 405 nm to 980 nm. (b, c) I - t curves of HfS₃ nanobelts under 405-nm and 980-nm light with an on-off period of 1 s at a bias voltage of 5 V, respectively. (d) I - V curves of HfS₃/GO under dark and illumination with the wavelength range from 405 nm to 980 nm. (e, f) I - t curves of HfS₃/GO under 405-nm and 980-nm light with an on-off period of 1 s at a bias voltage of 5 V, respectively. (g) I - V curves of HfS₃/RGO under dark and illumination with the wavelength range from 405 nm to 980 nm. (h, i) I - t curves of HfS₃/RGO under 405-nm and 980-nm light with an on-off period of 1 s at a bias voltage of 5 V, respectively.

Fig. 6. I - t curves of the photodetectors under 405-nm light at the bias of 5 V after the

six photodetectors were placed for 3 months and bended 500 times. (a) HfSe_3 nanobelts, (b) HfSe_3/GO composite, (c) HfSe_3/RGO composite, (d) HfS_3 nanobelt, (e) HfS_3/GO composite, (f) HfS_3/RGO composite.

Table 1 Comparison of HfSe₃, HfS₃, HfSe₃/GO (RGO) and HfS₃/GO (RGO) photodetectors at 405 nm with 14.4 mW/cm²

Photodetectors	R ₄₀₅ (mA/W)	EQE(%)	Rise/decay time (s)	I _{on/off}
HfSe ₃ NBs	1.1×10^{-4}	3.32×10^{-5}	0.82/0.57	1.22
HfSe ₃ NBs/GO	4.3×10^{-3}	1.3×10^{-3}	0.66/0.7	1.01
HfSe ₃ NBs/RGO	0.5	0.15	0.71/0.77	1.06
HfS ₃ NBs	0.11	3.43×10^{-2}	0.2/0.14	17.99
HfS ₃ NBs/GO	0.92	0.28	0.14/0.17	1.13
HfS ₃ NBs/RGO	0.55	0.17	0.51/0.45	1.04

Table 2 Comparison of HfSe₃, HfS₃, HfSe₃/GO (RGO) and HfS₃/GO (RGO) photodetectors at 980 nm with 34.4 mW/cm²

Photodetectors	R ₄₀₅ (mA/W)	EQE(%)	Rise/recovery time (s)	I _{on/off}
HfSe ₃ NBs	1.25×10^{-6}	1.58×10^{-7}	0.66/0.4	1.03
HfSe ₃ NBs/GO	7.2×10^{-5}	9.13×10^{-6}	0.83/0.53	1.003
HfSe ₃ NBs/RGO	1.2×10^{-2}	1.52×10^{-3}	0.78/0.61	1.02
HfS ₃ NBs	1.51×10^{-4}	1.92×10^{-5}	0.22/0.53	1.36
HfS ₃ NBs/GO	1.68×10^{-3}	2.13×10^{-4}	0.4/0.73	1.003
HfS ₃ NBs/RGO	7.57×10^{-3}	9.6×10^{-4}	0.54/0.68	1.01

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig.6

Graphical Abstract