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Quantum dot nanocolumn photodetectors for light detection in the infrared
Highly sensitive photodetectors based on hybrid 2D-0D SnS₂-copper indium sulfide quantum dots

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Both high speed and efficiency of photoelectric conversion are essential for photodetectors. As an emerging layered metal dichalcogenide (LMD), tin disulfide owns intrinsic faster photodetection ability than most other LMDs but poor light absorption and low photoelectric conversion efficiency. We develop an efficient method to enhance its performance by constructing a SnS₂-copper indium sulfide hybrid structure. As a result, the responsivity reaches 630 A/W, six times stronger than pristine SnS₂ and much higher than most other LMDs photodetectors. Additionally, the photocurrents are enhanced by more than 1 order of magnitude. Our work may open up a pathway to improve the performance of photodetectors based on LMDs. © 2016 AIP Publishing LLC.

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Earth-abundant layered metal dichalcogenides (LMDs) with general formula MX₂ (M = Mo, W, Sn, Ti, Zr, Hf, Nb, Ta, and X = S, Se) have attracted a great deal of attention over the past decade. The nature of suitable band-gaps and monolayer-stability enable them ideal candidates for application in photodetection, which require high performance in terms of speed and efficiency of photoelectric conversion. Motivated by those targets, a great number of photodetectors based on LMDs, such as MoS₂ and WSe₂, have been fabricated. However, a few of them can meet both. As an important member of LMDs, tin disulfide (SnS₂) has attracted increasing attention recently. Field effect transistors (FETs) based on exfoliated SnS₂ Nanosheets (NSs) show high on/off ratio ≈10⁶ and mobility up to 230 cm² V⁻¹ s⁻¹ at room temperature. Monolayer to few-layer SnS₂ NSs have been synthesized by chemical vapor deposition (CVD) on carbon fiber, mica, and silicon substrates. SnS₂ NSs especially can behave similar to ultrastack photodetectors with the rising time ≈ 5 μs, which is at least an order of magnitude faster than those based on MoS₂, WSe₂, GaTe, and many other layered materials, indicating its great superiority as ultra-sensitive photodetectors. However, its responsivity is limited to 8.8 mA/W. Recently, we synthesized thin SnS₂ NSs on carbon fibers through a CVD method and verified its potential in fast and sensitive phototransistors. But the indirect bandgap nature of SnS₂ may hinder the photoelectric conversion efficiency from achieving a higher standard. Thus, it is of great value to explore a strategy that improves the light absorption of SnS₂ photodetectors.

On the other hand, 2D-0D hybrid architectures have recently received considerable attention for their high performance as photodetectors. This structure benefits from strong light absorption, facile bandgap tunability, large scale manufacturability of quantum dots (QDs), and the facilitative separation of photoexcited charges induced by type II heterojunction formed between the QDs and the layered materials. Besides, with the single crystal layered material as a channel, this structure also avoids the boundary issues in QDs photodetectors. As a result, the responsivity of the hybrid graphene-PbS phototransistors could be 10⁷ A/W with fast response time ≈10 ms. A hybrid MoS₂-PbS QDs photodetector could show high responsivity of 10⁹ A/W as well as fast response time ≈0.35 ms. Accordingly, we designed a hybrid device combined p-type copper indium sulfide (CuInS₂, CIS) QDs with the CVD-grown SnS₂ NSs. The schematic of the hybrid device is shown in Fig. 1(a). The CIS QDs have demonstrated fruitful application in solar cell for its high light absorption and chemical stability. Besides, with its proper energy band structure, CIS-decorated SnS₂ could form a typical type-II band alignments, as shown in Fig. 1(b), which helps to improve photoresponse of SnS₂.

Herein, we report a photodetector based on SnS₂-CIS QDs hybrid architecture. Due to the type II heterojunction formed between SnS₂ and CIS QDs, the device exhibits enhanced light absorption ability, fast photoresponse, sensitive and gate-tunable photodetection. It is also notable that the responsivity reaches as high as 630 A/W at P = 2.83 mW/cm², which is comparable with that of graphene-PbS hybrid photodetection at the same power of illumination. Thus, our study may provide a method to improve the performance of photodetectors and expand the building blocks for high performance optoelectronic devices.

The SnS₂ NSs were synthesized by a CVD method as reported in our previous work. The CIS QDs were synthesized through a solvothermal recipe. In a typical process, 0.33 g CuCl₂, 0.81 g InCl₃, and 1.04 g SC(NH₂)₂ were added to 3 ml alcohol and 40 ml deionized water in a 50 ml Teflon autoclave. Then the reactor was maintained at 240 °C for 3 h. After that, ~10 nm CIS QDs were precipitated at the bottom of the reactor. To fabricate device, as-grown thin SnS₂ NSs were drop-casted onto p-doped silicon substrates with 300 nm thick thermal oxidation layer. A standard e-beam...
lithography (EBL) process was carried to define the electrical metal electrodes. Cr/Au (5 nm/80 nm) metal electrodes were deposited by thermal evaporation. After the measurement of pristine SnS$_2$ device, CIS QDs were spin-coated onto its surface, using a method similar with Ref. 17. During this procedure, 20 mg CIS QDs were dissolved in 5 ml toluene and centrifuged at 3000 rpm for 30 s. Then two drops (each drop $\sim$0.05 ml) of the supernatant was dropped onto the rotating substrates (2000 rpm) followed by 2 drops of 2 vol. % 1,2-ethanediol-ligands (EDT) in acetonitrile and another 2 drops of acetonitrile and toluene. This sequence was repeated for 3 times. Then, the substrate was dried at 30 °C for 10 min.

Transmission electron microscope (TEM) and Raman spectrum were used to characterize our synthesized SnS$_2$ nanosheets and CIS QDs. Fig. 1(c) exhibits the HRTEM of the SnS$_2$ NSs (top panel) and CIS QDs (bottom panel). The high crystallinity of the SnS$_2$ NSs could be concluded from the regular diffraction fringes with the lattice spacing of 3.15 Å indexed to the (100) plane. Meanwhile, the lattice constant $\sim$3.18 Å in Fig. 1(e) (bottom panel) agrees well with the (112) plane of CIS. Raman spectra of SnS$_2$ NSs, CIS QDs, and the hybrid structure are shown in Fig. 1(d), respectively. It is clear that the Raman spectrum of the hybrid structure shows two peaks assigning to that of SnS$_2$ nanosheets (313.6 cm$^{-1}$) and CIS (303.2 cm$^{-1}$). The UV-visible-IR absorption spectroscopy of SnS$_2$ and hybrid SnS$_2$-CIS quantum dots in Fig. 1(e) verifies that the light absorption range of hybrid SnS$_2$-CIS is enhanced and extended to part of the near infrared (NIR) region after CIS QDs deposition.

To investigate the performance of SnS$_2$-CIS hybrid photodetector, photoresponse of the pristine and hybrid device under 473 nm laser were conducted, respectively. Noting that our previous work has demonstrated oxygen molecules under build-in field between the interface of CIS and SnS$_2$ drive the photogenerated electrons and holes to move in opposite directions, reducing the recombination rate significantly. The electrons transferred from CIS to SnS$_2$ can increase the charge density of the channel material, leading to higher photocurrents. Meanwhile, the holes are trapped in the CIS built-in field between the interface of CIS and SnS$_2$ drives the photogenerated electrons and holes to move in opposite directions. As plotted in Fig. 2(c), the highest responsivity of the hybrid device reaches as high as 167 A/W, while that of the pristine device is 167 A/W. The time-resolved photoresponse of the device (Fig. 2(d)) shows that after QDs deposition, the rising and decay time could remain within 110 ms. Meanwhile, no obviously slow decay tail was observed, indicating the potential of the hybrid device for sensitive photodetectors. Here, the enhanced photocurrents and responsivity origin from the designed type II structure. Band bending induced by the current of hybrid device slightly increase while the photocurrents dramatically augment by at least one order. This increase could also be verified by the photoresponse of the hybrid and pristine device under different power of incident illumination, as shown in Fig. 2(b) After decorating with CIS QDs layer, the sensitivity of the SnS$_2$ device remained, embodying in the increasing photocurrents as the power of incident illumination increases. Furthermore, as a critical parameter for photodetector, the responsivity ($R_s$) of the device was improved. The $R_s$ can be calculated as the following formula:

$$R_s = \frac{I_{ph}}{PS},$$

where $I_{ph}$ is the photocurrents and $P$ and $S$ are effective illumination intensity and area. As plotted in Fig. 2(c), the highest responsivity of the hybrid device reaches as high as 630 A/W at $P = 2.83$ mW/cm$^2$, while that of the pristine device is 167 A/W. The time-resolved photoresponse of the device (Fig. 2(d)) shows that after QDs deposition, the rising and decay time could remain within 110 ms. Meanwhile, no obviously slow decay tail was observed, indicating the potential of the hybrid device for sensitive photodetectors. Here, the enhanced photocurrents and responsivity origin from the designed type II structure. Band bending induced build-in field between the interface of CIS and SnS$_2$ drives the photogenerated electrons and holes to move in opposite directions, reducing the recombination rate significantly. The electrons transferred from CIS to SnS$_2$ can increase the charge density of the channel material, leading to higher photocurrents. Meanwhile, the holes are trapped in the CIS.
film, which further serve as an effect of photogating and lead to the transfer threshold voltage shift. It could also explain the background photocurrents change shown in Fig. 2(b). As shown in our previous work, SnS$_2$ displays great potential as phototransistors with sensitive light response and gate tunable photoswitch ratio. We further verify that its performance could be improved with hybrid architecture. Transfer curves with or without light illumination were measured before and after QDs deposition. Considering possible gate hysteresis, all the curves are acquired as the gate voltage was applied from negative to positive values. The hybrid device shows increased currents both in the dark and under illumination, as presented in Fig. 3(a). Besides, the threshold voltage shifts from 19.9 V to 8.81 V after QDs deposition, indicating an obvious electron doping effect. It is notable that our hybrid device exhibits positive photoconductivity in the whole range of gate sweeping, significantly different with Ref. 18, in which the MoS$_2$-PbS QDs photodetectors exhibit positive photoconductivity only at strong negative V$_{gs}$. As plotted in Fig. 3(b), the hybrid device remains sensitive photoresponse compared with the pristine device, showing increasing currents as the power of illumination increases. Even though the pristine device shows a relatively higher responsivity than many other LMDs, the responsivity of the hybrid device is still improved by several to ten times. Figs. 3(c) and 3(d), respectively, depict the responsivity of device before and after CIS QDs deposition as the power of illumination increases. We draw these two figures in the same range (10$^1$ mA/W–10$^6$ mA/W) to facilitate a comparison. The highest responsivity measured of hybrid phototransistors is 500 A/W at $P = 5.94$ mW/cm$^2$, $V_{gs} = 50$ V. Though several other hybrid devices have shown a responsivity as high as 10$^7$ A/W, the results were measured at a very low intensity of illumination. Our results are comparable with that of those hybrid phototransistors at the same intensity of illumination. Besides, it is obvious that the measured responsivity displays a tendency of increasing as the intensity of illumination decreases. At higher illumination intensity, more photogenerated charges are separated, which induce an increasing reverse electric field. As a result, the build-in field is lowered, leading to accelerating charges recombination at the interface and dropping responsivity. Thus, it is safe to predict that our hybrid device would show even higher responsivity at an illumination of lower intensity.

Another interesting phenomenon is that the transfer curves shift as the intensity of illumination increases, as indicated in Fig. 3(b). For one reason, photogenerated electrons transfer from the CIS layer to SnS$_2$, which results in more electrons in the channel. For another reason, photogenerated holes remained in the CIS QDs layer, leading to a photogating effect, which further changes the conductance of the channel material through capacitive coupling. As a result, the threshold voltage of the hybrid device shifts to negative gate voltages. To clearly show these collaborative effects, we plot the threshold voltage shift as a function of light illumination in Fig. 4(a). Interestingly, the curve can be fitted very well with the following equation, which has been used for phototransistors before:

$$\Delta V_{th} = \alpha P^\beta,$$

(2)

where $\Delta V_{th}$ is the shift of threshold voltage, $P$ is the intensity of light illumination, and $\alpha$ and $\beta$ are the constant. Besides, it is well known that the channel current could be expressed as

$$I_{ds} = \frac{W}{L} \mu C_{ox} \left(V_G - V_T - \frac{V_D}{2}\right)V_D, \quad V_D \ll (V_G - V_T),$$

(3)

where $C_{ox}$ is the capacitance of the gate dielectric per unit area and $L$ and $W$ are the length and width of the channel material, respectively. Then, the photocurrent of the hybrid device could be expressed as...
Substitute Equation (4) into Equation (1), the responsivity could be expressed as

\[ R_{\lambda} = \frac{W}{L} \mu C_{ox} V_D P^{\beta} \theta^{-1}. \]  

(5)

Fig. 4(b) shows the responsivity of our hybrid device as a function of light illumination, which fits very well with Equation (5). According to our experimental results, \( \beta \approx 0.48 \) is higher than that of a PbS-graphene hybrid device.\(^{19} \) In general, the value of \( \beta \) indicates the efficiency of charges transfer from the layer of QDs to the channel material. It depends on the quality of interface between the CIS QDs layer and SnS\(_2\) NSs, the surface ligand used to prepare QDs solution, and the experimental process.\(^{39} \) Therefore, by carefully choosing the ligand and improving the experimental procedure, it is possible that the value of \( \beta \) and the responsivity of the hybrid device could be further improved.

In summary, a hybrid device with sensitive photoreponse, fast response time, and improved responsivity was fabricated by spin-coating CIS QDs layer onto the surface of SnS\(_2\) NSs. These improvements benefit from strong light absorption of CIS QDs and the type II heterojunction formed between SnS\(_2\) surface and CIS QDs. As a result, the photocurrents are enhanced by more than one order and the responsivity of the hybrid device is higher than 600 A/W. Besides, the experimental data of the responsivity at varied power of incident illumination agree very well with the theoretical equation. Our work may broaden the 2D-0D system and offer a method to improve the performance of optoelectronic devices based on LMDs.

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