Paper-based Broadband Flexible Photodetectors with van der Waals materials

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Article

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Abstract

Layered metal chalcogenide materials are exceptionally appealing in optoelectronic devices thanks to their extraordinary optical properties. Recently, their application as flexible and wearable photodetectors (PDs) have received a lot of attention. Herein, broadband and high-performance paper-based PDs were established in a very facile and inexpensive method by rubbing molybdenum disulfide (MoS$_2$) and titanium trisulfide (TiS$_3$) crystals on papers. Transferred layers were characterized by SEM, EDX mapping, and Raman analyses, and their optoelectronic properties were evaluated in a wavelength range of 405-810 nm. Although the highest and lowest photoresponsivities were respectively measured for TiS$_3$ (1.50 mA/W) and MoS$_2$ (1.13 μA/W) PDs, the TiS$_3$-MoS$_2$ heterostructure not only had a significant photoresponsivity but also showed the highest on/off ratio (1.82) and fast response time (0.96 s) compared with two other PDs. This advantage is due to the band offset formation at the heterojunction, which efficiently separates the photogenerated electron-hole pairs within the heterostructure. Numerical simulation of the introduced PDs also confirmed the superiority of TiS$_3$-MoS$_2$ heterostructure over the other two PDs and exhibited a good agreement with the experimental results. Finally, MoS$_2$ PD demonstrated very high flexibility under applied strain, but TiS$_3$ based PDs suffered from its fragility and experience a remarkable drain current reduction at strain larger than ± 0.33%. However, at lower strains, all PDs displayed acceptable performances.

Introduction

With the development of smart and Internet of Things (IoT) based technologies, great efforts have been made on wearable and flexible electronic devices which are mostly implemented on Polyethylene terephthalate (PET) and Polydimethylsiloxane (PDMS) substrates$^1$. However, in addition to high manufacturing costs and lack of biodegradability, their fabrication processes require advanced laboratory equipment, which obstruct their possible practical applications$^2$. Flexible paper-based electronic devices are a new class of high-performance devices that offer admirable properties with facile and low-cost fabrication processes, ending in lightweight and environmentally friendly devices that are very promising for the future of smart electronics$^3$–$^5$. Flexible photodetectors (PDs), as a member of this family, have received a great deal of attention, suitable for optoelectronic systems such as optical communications, environmental monitoring, and imaging$^6$.

Two-dimensional (2D) materials, especially the chalcogenides family, have been increasingly used in optoelectronic devices in recent years due to their adjustable band gap, high electrical conductivity, and effective light-matter interactions$^7$. Metal chalcogenide based PDs have shown high photoresponsivity, fast response time, and high quantum efficiency$^8$. Interestingly, their paper-based PDs also demonstrates such a high performance$^9$–$^{11}$. Sahatiya et al. fabricated a MoS$_2$-Carbon Quantum dot (CQDs) based PD on cellulose paper using a hydrothermal growth of MoS$_2$ and casting of CQDs$^{12}$. Their reported device showed a photoresponsivity of 18 mA/W in the visible region with a response time of ~0.57 s. Selamneni
et al. hydrothermally grown MoS$_2$ on cellulose paper followed by decorating with various metal nanoparticles (Au, Pt, and Pd)\textsuperscript{11}. The photoresponsivities and response times of the PDs were measured to be around 45–100 mA/W and 0.9–1.2 s in the visible range, respectively. Cordeiro et al. introduced near-infrared PDs by growing MoS$_2$ on cellulose paper using a hydrothermal technique. Their PD showed a photoresponsivity of about 200 mA/W and a response time of 3.7 s\textsuperscript{13}. However, majority of methods used for the fabrication of paper-based PDs are time-consuming, complex, and consisting wet procedures. In contrast, rubbing of bulk crystal on ordinary paper can be a potential alternative to facile realization of paper-based PDs through a simple, fast and completely dry process. As an example, Mazaheri et al. transferred MoS$_2$ flakes by rubbing the corresponding crystal on paper and reported a paper based PD with a photoresponsivity of 1.5 µA/W in a wavelength range of 365 to 940 nm\textsuperscript{14}.

In this work, MoS$_2$ and TiS$_3$ flakes were transferred on papers by rubbing their corresponding bulk crystals. Three types of MoS$_2$, TiS$_3$, and TiS$_3$-MoS$_2$ PDs were fabricated and their optoelectronic properties were carefully evaluated in the wavelength range of 405 to 810 nm. Based on the results, the highest photoresponsivity were measured for TiS$_3$ PDs and the lowest for MoS$_2$ PDs. In the case of TiS$_3$-MoS$_2$ (MoS$_2$ film was placed on top of the TiS$_3$ film and exposed to light), it exhibited a faster response time, and higher on-off ratio thanks to formation of band offset at semiconductor heterojunctions. Numerical simulations also confirmed the superiority of TiS$_3$-MoS$_2$ PDs over MoS$_2$ PDs. Moreover, to evaluate the flexible performance of the PDs, the introduced devices were bent on both positive and negative curvatures and their $I_{ds}$-$V_{ds}$ and photocurrent characteristics were measured under strain range of ± 0.27% to ± 0.54%. The results showed that MoS$_2$ PDs had high flexibility, but TiS$_3$ based PDs were associated with the decline of drain current and photodetection responsivity at applied strains larger than ± 0.33%.

**Results And Discussions**

SEM image and XRD analysis of the grown TiS$_3$ microcrystals are presented in Figure S1. Before transferring the flakes, the surface of paper was investigated by SEM and EDX measurements. As can be seen in Figure S2a, the paper is formed by stacked cellulose fibers and it presents deep gaps/voids between fibers. EDX analysis also confirms the presence of carbon (C), oxygen (O), calcium (Ca), silicon (Si), aluminum (Al), iron (Fe), sodium (Na), and manganese (Mg) in the raw paper where their atomic percentages are listed in the inset of Figure S2b.

Figure 1 shows the characterization of the deposited flakes on paper substrates. The schematic illustration of the TiS$_3$-MoS$_2$ heterostructure and its corresponding photograph are also presented in panels (a) and (b) of Fig. 1, respectively. Figure 1c exhibits the SEM image of the MoS$_2$ flakes on the paper. According to the figure, MoS$_2$ flakes cover the fibers and gaps between fibers of the paper. The deposited TiS$_3$ flakes are also presented in Fig. 1d in which the thickness of the film is measured to be ~10 µm. Moreover, the SEM image of the TiS$_3$-MoS$_2$ heterostructure is observed in Fig. 1e. Due to softness
and flexibility of MoS$_2$, it forms a smoother film than TiS$_3$ on paper, which is visible in Fig. 1e. The EDX analysis of MoS$_2$, TiS$_3$, and TiS$_3$-MoS$_2$ samples on papers is presented in Figs. 1f-g. By rubbing MoS$_2$ on the paper, the Mo and S elements becomes significant (Fig. 1f). The EDX analysis of TiS$_3$ sample also proves the presence of S and Ti elements according to Fig. 1g. SEM-EDX analysis of transferred TiS$_3$ flakes is also presented in Figure S3. In the case of TiS$_3$-MoS$_2$ film, dominant elements are S, Mo, and Ti (Fig. 1h). The C, O and Ca elements come from raw paper. Table S1 summarizes the element contents of all samples with their weight and atomic percentages.

Figure 2a exhibits the magnified SEM image of the TiS$_3$-MoS$_2$ film where the MoS$_2$ film is deposited on the TiS$_3$ film. However, some TiS$_3$ microcrystals may also appear on top of the film due to the rubbing process. The Raman spectra of MoS$_2$, TiS$_3$, and TiS$_3$-MoS$_2$ samples are also presented in Fig. 2b. For MoS$_2$, E$_{2g}^1$ and A$_{1g}$ peaks are found at 379 and 403 cm$^{-1}$, respectively$^{15}$. In the case of TiS$_3$, the 193, 385 and 627 cm$^{-1}$ peaks refer to A$_g$ and E$_g$ modes, respectively$^{16}$. There is also one additional peak located at 507 cm$^{-1}$, which refers to B$_{1g}$ peak of TiO$_2$$^{17}$. This oxide peak may have appeared during the growth of TiS$_3$ microcrystals in the ampoule process. The Raman spectrum of TiS$_3$-MoS$_2$ sample contains all peaks of both structures. Figure 2c shows the mapping analysis of the TiS$_3$-MoS$_2$ sample where the dominant elements are separately shown in Fig. 2d. Accordingly, O, C, and Ca elements are due to the raw paper, and elements of Ti, Mo, and S originate from the TiS$_3$ and MoS$_2$ films. It can be seen that all elements are uniformly distributed on the paper.

To investigate the optoelectronic properties of the films, MoS$_2$, TiS$_3$, and TiS$_3$-MoS$_2$ PDs were fabricated. Details of their fabrication are provided in the experimental section. The fabrication steps of MoS$_2$ and TiS$_3$ PDs are shown in Figures S4 and S5, respectively. In the case of TiS$_3$-MoS$_2$ PD, the fabrication steps are presented in Fig. 3.

Panels (a) to (c) of Fig. 4 display I-V characteristics of the MoS$_2$, TiS$_3$, and TiS$_3$-MoS$_2$ PDs at a bias range of -10 to +10 V in dark and under 532 nm laser illumination at different power intensities. In all three PDs, significant photocurrents were generated compared to the dark state. The incident power is normalized in terms of laser spot and PD’s channel areas. Accordingly, the effective incident power is calculated as:

$$P_{\text{eff}} = P_{\text{laser}} \times A_{\text{device}} / A_{\text{laser}} \quad (1)$$

Where $P_{\text{laser}}$ is the power of the laser, $A_{\text{device}}$ is the area of the PD’s channel, and $A_{\text{laser}}$ is the area of the laser spot. The diameter of the 532 nm laser spot was 2.81 mm and its area ($A_{\text{laser}}$) was measured to be 6.22 mm$^2$. As the laser intensity increases, the photocurrent also increases for all three PDs. In detail, the drain currents were measured in the range of $\sim 0-4$ nA, $\sim 0-8$ µA and $\sim 0-450$ nA for MoS$_2$, TiS$_3$, and TiS$_3$-MoS$_2$ PDs at a biasing voltage of 0–10 V, respectively. Interestingly, the $I_{ds}$ in TiS$_3$-MoS$_2$ is significantly higher than that of individual MoS$_2$, which indicates the effective role of the band offset formation in increasing the photocurrent. The I-V curves of the all PDs in response to 405, 655, and 810
nm laser illuminations are also shown in Figure S6 where all PDs respond to the laser irradiation by an increase in current. Figure 4d-i compare the photocurrent and photoresponsivity of all three PDs at different power intensities of 532 nm at an applied voltage of 10 V. According to Fig. 4d-f, with increasing effective incident power (from zero to a few mW), increase in the photocurrents are occurred. In the MoS$_2$ PD, the photocurrent increases to about 1.6 nA. For TiS$_3$, this value is more noticeable and a 1.0 µA increase of photocurrent is observed. In the case of TiS$_3$-MoS$_2$ PD, photocurrent increases up to 300 nA. The photoresponsivity of the PDs are calculated based on the following Eq. 1:

$$ R = \frac{I_{ph}}{P_{eff}} \quad (2) $$

Where $I_{ph}$ is the photocurrent of the PDs. In the MoS$_2$ PD, increasing the effective power associates with decrease of the photoresponsivity. The same trends are also observed for TiS$_3$, and TiS$_3$-MoS$_2$ PDs. As the incident power increases, more photocarriers are generated, which increases the recombination rate of photogenerated carriers or the possibility of being captured by the traps, leading to a decrease in $R$\textsuperscript{19,20}. In general, the photoresponsivities are measured in the range of 0.4–1.2 µA/W, 0.4–1.6 mA/W, and 90–170 µA/W for MoS$_2$, TiS$_3$, and TiS$_3$-MoS$_2$ PDs, respectively. Accordingly, the photoresponsivity of the last two PDs is three and two orders of magnitude greater than that of MoS$_2$ PD.

Figure 5a-c show the measured photocurrent in terms of the different effective powers of the 532 nm laser. Accordingly, an increase in the optical powers leads to an increase in photocurrent in all PDs. Panels (d) to (f) of Fig. 5 display the time trace response of the PDs to 532 nm laser illumination at a drain voltage of 10 V at an incident power of 10 mW. Rise time ($\tau_{on}$) is defined as the time taken to increase the current from 10–90% of its baseline under laser illumination\textsuperscript{21}. The fall time ($\tau_{off}$) is the time required to reduce the current from 90–10% of its baseline\textsuperscript{22}. For MoS$_2$, the rise and fall times are measured to be 2.17 and 9.99 s, respectively. In the TiS$_3$ PD, the $\tau_{on}$ and $\tau_{off}$ of 2.4 and 17.44 s are measured and in the TiS$_3$-MoS$_2$ PD, $\tau_{on}$ and $\tau_{off}$ of about 0.96 and 8.42 s are calculated that it shows faster switching performance compared with two other PDs.

Figure 6a compares the photoresponsivity of several fabricated PDs at an applied voltage of 10 V under a laser wavelength of 532 nm. It is observed that all three TiS$_3$ PDs have the highest photoresponsivity, followed by TiS$_3$-MoS$_2$ and MoS$_2$ samples, respectively. In general, the $R$ are measured in the range of 0.67–1.56 mA/W for TiS$_3$ PDs and 0.20–1.93 µA/W in the case of MoS$_2$ PDs. For TiS$_3$-MoS$_2$ PDs, these values are measured in the range of 0.08 to 0.19 mA/W. Accordingly, MoS$_2$ has the lowest photoresponsivity and TiS$_3$ possess the highest photoresponsivity. However, both photoresponsivity and photocurrent of TiS$_3$-MoS$_2$ PDs are considerable compared to the MoS$_2$ PD. Moreover, a similar trend is observed in the order of magnitude of all calculated $R$ in these PDs. Figure 6b shows the photoresponsivity of all three devices in terms of different laser wavelengths at the same power of 15 mW and supply voltage of 10 V. All three PDs have a broad response within the range of 400 to 800 nm. The photoresponsivity of the TiS$_3$ PDs are one order of magnitude greater than that of the TiS$_3$-MoS$_2$
PDs and two orders greater than that of the MoS$_2$ PDs. Figure 6c compares the measured $I_{on}/I_{off}$ ratio and dark current of all three PDs under 532 nm laser irradiation. The error line shows the deviation of the values obtained for the same PDs. The on-off ratio ($I_{on}/I_{off}$) is usually used to describe the signal-to-noise ratio$^{23}$. According to Fig. 6c, the values of 1.35, 0.17, and 1.82 are obtained for MoS$_2$, TiS$_3$, and TiS$_3$-MoS$_2$ PDs, respectively. Based on them, the highest signal-to-noise ratio is related to the TiS$_3$-MoS$_2$ PDs. Interestingly, the dark currents are lowest in MoS$_2$ ($\sim$ 1.2 nA) and highest in TiS$_3$ ($\sim$ 6.0 µA). Since the light detection mechanism is based on the change of drain current in these PDs, less dark current provides better performance in light detection as will be discussed below$^{24}$. Another important parameters are the rise and fall times which are presented in Fig. 6d. Accordingly, the TiS$_3$-MoS$_2$ PD has the fastest response time to laser radiation than the other two PDs. Figure 6e shows the energy band diagram of the TiS$_3$-MoS$_2$ heterostructure and its corresponding photodetection mechanism. TiS$_3$ is an n-type semiconductor with an energy band gap of 1.1 eV and MoS$_2$ is also an n-type semiconductor with an energy band gap in the range of 1.2–1.8 eV$^{25,26}$. Here, the energy band gap of bulk MoS$_2$ is considered because most layers are thick, although the deposited film can contain single and few layers of MoS$_2$. The electron affinities of MoS$_2$ and TiS$_3$ are around 4 and 4.7 eV, respectively, and hence the conduction band of TiS$_3$ is located of MoS$_2$, forming an n-n$^+$ heterostructure$^{27,28}$. In the MoS$_2$ film under laser irradiation, electron-hole pairs are generated and the photogenerated electrons enter into the TiS$_3$ due to its lower conduction band which prevents electrons from recombination with the holes. Moreover, the valence band of MoS$_2$ is located higher than that of TiS$_3$ resulting in transferring of minority holes from TiS$_3$ into MoS$_2$. Hence, the recombination rate of the carriers is decreased in the heterostructure. Such charge separation in the heterostructure is responsible for faster response time, and improved photoresponsivity of the heterostructure compared with individual MoS$_2$ PDs.

Since the substrate is made of paper, the performance of the introduced PDs was thoroughly investigated under applied strain. For this purpose, a homemade setup was fabricated to apply strain to the substrates as shown in Figure S7. This setup includes a cage covered with aluminum foil to act as a Faraday cage. The sample is fixed to a motor shaft through a hook to provide upward and downward strains by moving in a clockwise or counter-clockwise direction. The strain applied to the PDs was calculated according to $\varepsilon = t/2R$ equation, where $t$ is the thickness of the substrate and $r$ is the radius of bending curvature$^{29}$. Figure S8 presents the applied strains in the PDs, which are performed in the range of -0.54% to + 0.54%. As can be seen, at strains larger than ± 0.33%, a significant bending is occurred in the substrates.

Figures 7a and 7b show the schematic of applying the upward and downward strain in the PDs under exposing to 532 nm laser illuminations, respectively. Panels (c), (d), and (e) of Fig. 7 compare the $I_{ds}$-V curves of the MoS$_2$, TiS$_3$, and TiS$_3$-MoS$_2$ PDs in the flat state and under negative and positive strains, respectively. For the MoS$_2$ sample, it is observed that the drain current in the flat state almost remains the same as under different applied strains without any significant change. The flexible and soft structure of MoS$_2$ is the main reason for this behavior$^{30}$. For TiS$_3$, it is found that the $I_{ds}$ decreases after applying
downward strains, but a more significant decrease is observed in the upward strains. Moreover, after upward strain, by returning the TiS$_3$ to its flat position, current does not return to its original value of before any strain. The structure of TiS$_3$ is more fragile than that of MoS$_2$, and bending can break the contact between TiS$_3$ and Ag paste, affecting the conductivity$^{31}$. As a result, even after the sample has returned to the flat state, the current dramatically suffers from decline. A similar trend is observed in the TiS$_3$-MoS$_2$ PD, but with a more noticeable decrease after positive strains, which could be due to the separation of the two films at the interface and the reduction of the electric field in the channel. Figures 7f-h show the photocurrent characteristics of all PDs under 532 nm laser irradiation at a drain voltage of 10 V and an incident power of 15 mW. For MoS$_2$ PD, the photocurrent is well switched under negative and positive strains of 0.33% similar to the flat state. In the case of TiS$_3$, the photocurrent decreases in both applied strains of -0.33% and +0.33%, but TiS$_3$-MoS$_2$ shows a more noticeable decrease compared to its flat state. As discussed, the brittle structure of TiS$_3$ as well as the separation of the two films at the junction, especially at a strain of +0.33%, play important roles in this performance deterioration of the TiS$_3$ based PDs.

Numerical simulation is employed to present further insight about the physics of light-induced generation-recombination processes for charged carriers in these devices. We used the model to calculate the photocurrent of the devices in response to the incident light under various biasing conditions. Details of the simulation can be found in the supporting information section. Panels (a) to (c) of Fig. 8 depict the schematic of the devices consisting MoS$_2$, TiS$_3$ and heterostructure with stacked layers of both materials. Overlapped part in the heterostructure device was exposed to the incident light with the wavelength of 532 nm. Stray electromagnetic field due to unintentional exposure is also took into the account. Corresponding light-induced electric field can be seen in Fig. 8d for all devices due to laser exposure. Vertical electric field was established by applying a voltage difference between the two terminals at both ends, where contacts are located. Figure 8e-f show the electron and hole concentrations under this biasing condition in a logarithmic scale, respectively. As can be seen, the distribution of electrons and holes in the two structures of MoS$_2$ and TiS$_3$ is almost uniform, but in the TiS$_3$-MoS$_2$ device, the band offset accelerates the separation of electrons and holes and causes a non-uniform distribution of carriers at the two-layer boundary. These results indicate that the formed n-n + heterostructure can more efficiently separate the charge and confirms its superior optoelectronic performance compared with the individual MoS$_2$ case.

At various light intensities, I-V characteristic curves has been simulated for MoS$_2$, TiS$_3$, and TiS$_3$-MoS$_2$ photodetectors. The obtained curves for drain currents are consistent with the measurements as illustrated in Figure S9a-c. Relative differences between the amplitude of photocurrent is in all devices is in total agreement with the experiments where TiS$_3$ and MoS$_2$ PDs have higher and lower photocurrents, respect to the hybrid structure under identical biasing and light exposure conditions.

Table 1 compares the performance of the introduced PDs with some other reported paper-based PDs. According to it, most of them have a photoresponsivity in the range of a few µA/W. In the case of MoS$_2$,
is observed that our introduced PD has a slightly higher photoresponsivity than the others. The TiS$_3$ PD shows a much higher photoresponsivity (in the range of mA/W), which has a significant improvement in performance compared to other reported PDs. However, it shows a larger dark current and a smaller on/off ratio than MoS$_2$ PDs which can limit its optical detection performance. Finally, the photoresponsivity of the TiS$_3$-MoS$_2$ heterostructure shows a significant improvement, which indicates its superiority over other works.

Table 1
Comparison of the performance of introduced paper-based PDs with other PDs based on different 2D materials.

| Paper-based PDs     | $V_{ds}$ | $\lambda$ | $R$   | ref |
|---------------------|----------|-----------|-------|-----|
| Te—TiO$_2$          | 0 V      | 400 nm    | 30 µA/W | 32  |
| ZnS-MoS$_2$         | 1 V      | 554 nm    | 18 µA/W | 33  |
| MoTe$_2$            | 1 V      | 532 nm    | 1.1 µA/W | 34  |
| MoSe$_2$            | 1 V      | 532 nm    | 0.2 µA/W |
| WS$_2$              | 1 V      | 532 nm    | 0.06 µA/W |
| MoS$_2$             | 1 V      | 532 nm    | 0.02 µA/W |
| MoS$_2$             | 20 V     | 532 nm    | 1.1 µA/W | 14  |
| MoS$_2$             | 10 V     | 532 nm    | 1.2 µA/W |
| TiS$_3$             | 10 V     | 532 nm    | 1600 µA/W |
| TiS$_3$-MoS$_2$      | 10 V     | 532 nm    | 170 µA/W |

Conclusions

The two-dimensional (2D) layered family of transition metals chalcogenides shows high potential as photodetectors because they not only interact effectively with light but also provide high carrier transport properties. In this report, a very simple, fast and promising clean method is introduced to fabricate the paper-based photodetectors using MoS$_2$, TiS$_3$ and their integration. The all introduced photodetectors show remarkable photoresponsivities in the range of 405 to 810 nm. In the case of TiS$_3$-MoS$_2$ heterostructure, it associates with fast response time and large on-off ratio compared to individual MoS$_2$ and TiS$_3$ photodetectors. The numerical simulation results are consistent with the experimental results and confirm the superiority of the hybrid structure over the two other PDs. Moreover, the bending results of the photodetectors indicate that in applied strains smaller than ± 0.33%, these devices still show acceptable performance.
Methods

Material: Naturally occurring molybdenite crystal, from Wolfram Camp Mine, Queensland, Australia, were used. Silver paste was purchased from Dycotec Materials, UK DM-SIP-3060S. Ordinary papers (CopiMax, Thailand) were used as substrates.

TiS$_3$ preparation: TiS$_3$ microcrystals were synthesized by a solid-gas reaction of titanium powder through direct sulfurization. In detail, titanium powder (Goodfellow, > 99% purity) and sulfur powder (Merck, > 99.9% purity) were vacuum sealed in an ampule and heated up to 500 °C for 20 hours. Then, the ampule was cooled down to room temperature and grown microcrystals were collected.

Fabrication of MoS$_2$ (TiS$_3$) paper-based photodetector: First, a piece of paper with 2×6 cm$^2$ dimensions was cut and attached on a slide glass using adhesive tape. A shadow mask (a 1×6 mm$^2$ rectangular window) was then opened in the center of the paper with adhesive tape. A piece of bulk MoS$_2$ (or TiS$_3$) was rubbed several times along the length and width of the open-window reign. After deposition of a homogeneous layer of MoS$_2$ (TiS$_3$), the mask was removed from the paper. Silver paste was then placed on the both sides of the deposited film, and two pieces of soft copper wire were mounted on the paste and kept at room temperature for 24 hours for improving the adhesion. Then, the dried silver paste was covered with epoxy glue for strengthening and achieving higher mechanical stability. The photograph of the fabrication steps of MoS$_2$ and TiS$_3$ PDs are presented in the supporting file.

Fabrication of TiS$_3$-MoS$_2$ paper-based photodetector: First, a piece of paper with a dimension of 2×6 cm$^2$ was cut and attached to a slide glass. A rectangular shadow mask (mask 1) was opened by the adhesive tape in the center of the paper. With the use of another mask (mask 2), this part was divided into two sections with dimensions of 1×4 mm$^2$ (for TiS$_3$ deposition) and 1×2 mm$^2$ (for MoS$_2$ deposition). A piece of bulk TiS$_3$ was rubbed several times in the open-window region. Then, mask 2 was removed from the paper and MoS$_2$ crystal was finger-rubbed several times on the 1×2 mm$^2$ part of the bare paper and 1×1 mm$^2$ part of the deposited TiS$_3$. Thus, the center of the sample (device) with dimensions of 1×1 mm$^2$ was a film composed of TiS$_3$ and MoS$_2$, in which TiS$_3$ was placed beneath the MoS$_2$ film. After removing mask 1 from the paper, a homogeneous film composed of TiS$_3$, MoS$_2$ and, TiS$_3$-MoS$_2$ with dimensions of 1×3, 1×1, and 1×1 mm$^2$ can be achieved, respectively. Similar to previous PDs, copper wires were added to both sides of the film. The TiS$_3$-MoS$_2$ PD is ready for testing.

Characterizations: SEM images and EDX analyses were taken by TESCAN MIRA 3 and EDX (Energy-dispersive X-ray) systems. Crystalline structure was identified by using a Panalytical X’Pert Pro X-ray diffractometer at glancing angle configuration (incident angle of 1.7º) with CuK$\alpha$ radiation. Raman spectra of the transferred flakes were measured by Avantes (AVASPEC-ULS3648-RS) system under 532 nm laser illumination. Electrical measurements were carried out by a Keithley 2450 source meter. Optical measurements were done under different laser excitations including 405, 532, 655, and 810 nm at room
temperature in air ambient. Bending tests were performed with a homemade setup capable of applying both upward and strains.

**Declarations**

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**Figures**

**Figure 1**

**a)** Schematic illustration of the TiS3-MoS2 film on the paper. **b)** Photograph of the fabricated TiS3-MoS2 film on the paper. SEM image of the transferred **c)** MoS2, **d)** TiS3, **e)** TiS3-MoS2 flakes on the paper. EDX analysis of the **f)** MoS2, **g)** TiS3, and **h)** TiS3-MoS2 films on the paper.

**Figure 2**
Characterization of the TiS$_3$-MoS$_2$ film on the paper. a) SEM image of the film. b) Raman spectra of the MoS$_2$, TiS$_3$, and TiS$_3$-MoS$_2$ films. c) Mapping analysis of the TiS$_3$-MoS$_2$ sample on the paper. d) Elemental mapping of six dominant elements in the TiS$_3$-MoS$_2$ sample.

Figure 3

Fabrication steps of the TiS$_3$-MoS$_2$ PD.
Figure 4

I-V characteristics of the a) MoS$_2$, b) TiS$_3$, and c) TiS$_3$-MoS$_2$ PDs under 532 nm laser illumination at different power intensities. Photocurrent versus incident power intensity for d) MoS$_2$, e) TiS$_3$, and f) TiS$_3$-MoS$_2$ PDs under 532 nm laser illumination at an applied voltage of 10 V. Photoresponsivity versus incident power intensity for g) MoS$_2$, h) TiS$_3$, and i) TiS$_3$-MoS$_2$ PDs under 532 nm laser illumination at a supply voltage of 10 V.

Figure 5

The measured photocurrent as a function of laser intensities for a) MoS$_2$, b) TiS$_3$, and c) TiS$_3$-MoS$_2$ PDs under 532 nm laser illumination at a constant voltage of 10 V. Time trace measurement of d) MoS$_2$, e) TiS$_3$, and f) TiS$_3$-MoS$_2$ PDs under 532 nm laser illumination at an applied voltage of 10 V and laser intensity of 10 mW. The corresponding $P_{eff}$ was calculated to be 1.53 mW, 1.03 mW, and 1.39 mW for panels (d) to (f), respectively.
Figure 6

Comparison of a) photoresponsivity as a function of the incident power for several fabricated PDs at an applied voltage of 10 V under a laser wavelength of 532nm, b) the photoresponsivity of fabricated PDs under various laser wavelengths at an applied voltage of 10 V, c) $I_{on}/I_{off}$ and dark current, d) rise and fall times of the MoS$_2$, TiS$_3$, TiS$_3$-MoS$_2$ PDs at a constant voltage of 10 V, and e) Energy band diagram and detection mechanism in the TiS$_3$-MoS$_2$ heterojunction.
Figure 7

Schematic illustrations of a) upward and b) downward applied strains at the PDs under laser illuminations. I<sub>dS</sub>-V curves of the c) MoS<sub>2</sub>, d) TiS<sub>3</sub>, and e) TiS<sub>3</sub>-MoS<sub>2</sub> PDs under different applied strains. Photocurrent switching performance of the f) MoS<sub>2</sub>, g) TiS<sub>3</sub>, and h) TiS<sub>3</sub>-MoS<sub>2</sub> PDs in flat state and at applied strains of ±0.33% under 532 nm laser illumination at a bias voltage of 10 V.
Figure 8

Schematic illustrations of device geometries for a) MoS₂ b) TiS₃ and c) TiS₃-MoS₂ heterostructure, d) exposed surface of the devices and light-induced electric field, e) electron and f) hole concentrations in a logarithmic scale for the three devices.

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