A robust 3D self-powered photoelectrochemical type photodetector based on MoSe2 nanoflower

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ABSTRACT

Molybdenum selenide (MoSe2) has been extensively studied in recent years due to its strong absorption for sunlight and unique band structure. Herein, a self-assembly three-dimensional (3D) MoSe2 nanoflowers were prepared by a two-step process. Significantly, the photodetection device based on MoSe2 nanoflowers exhibited a maximum responsivity about 12.39 μA W−1 and a rapid photo-response time about 0.15 s at 0 V bias under simulated sunlight exposure benefiting from its large specific surface area and unique morphologic structure. Meanwhile, we demonstrated the outstanding stability after 2 weeks of the photodetection device. In this way, the MoSe2 nanoflower-based photodetectors enriched the basic research of molybdenum selenide and provided some reference for the following researches based on molybdenum selenide.

1 Introduction

The process of optical detection is a significant phenomenon of converting light into electrical signal that plays important roles in photoelectric device, chemical/biomedical sensors military and information communication [1–3]. Meanwhile, two-dimensional materials such as MoS2 [4], WSe2 [5], MoTe2 [6], MoSe2 [7] have been proved to be promising optoelectronic materials due to their unique growth structure and good photoelectric properties [8]. Among MeX2 structural formula, MoSe2 has become one of the promising candidate materials for near infrared photodetectors due to few-layer MoSe2 huge advantages such as direct band gap (monolayer or less) about 1.5 eV and high anti-photo corrosion stability, as well as the stronger absorption of sunlight [9–12]. The pretty superiority makes MoSe2 suitable for working in tough environment. Generally, most of photodetectors need to apply an external bias voltage to obtain considerable detection capability. Therefore, self-powered system is increasingly popular among researchers due to without external power supply, environment-friendly, low power consumption [13, 14].
Although researchers have made PDs based on nanosheets and nanofilms with wonderful performance, such as GeH nanosheets with excellent responsivity and rapid response time prepared by Liu et al. [15] and the ultrathin MoSe₂ films with almost perfect light absorption synthesized by Du et al. [16], there are still need to search for other techniques to meliorate their performance. Recently, researchers pay special attention to the development of new semiconductor materials, new structures of compounds, providing unique solutions to enhance current transmission and improve the performance of devices [17]. Researchers designed other structures such as nanoflowers, thin of nanosheets and branched nanorods to enhance the performance of device [18–20]. The nanoflower structures have been illustrated to improve the absorption of light through multiple refraction of light and number of active regions [21, 22]. PDs manufactured with such structure also exhibited fabulous reliability and sensitivity, low requirements and high-speed operations with quick response time [9]. Aggarwal et al. reported a self-powered photodetector-based GaN nanoflowers with increasing the active area for absorbing the incident photons due to high surface to volume ratio [7, 9]. And Song et al. [23] prepared the TiO₂ nanoflowers by hydrothermal method and the TiO₂ nanoflower-based photodetectors exhibited a great self-powered performance with eximious stability and repeatability. Foreseeably, the approach is effective to improve the light absorption of the device [21].

In this letter, we have prepared MoSe₂ nanoflowers with large specific surface area that make the absorption of incident light more adequate [9, 21] and large absorption area of incident photons and strong detection ability [23, 24], which was a kind of three-dimensional (3D) nanostructure [25, 26]. In addition, under the condition of global energy crisis, the independent and sustainable self-powered supply system is a necessary issue that has aroused the attention of researchers. The self-powered photodetectors presented the advantages of low power consumption and energy saving, which are very suitable for extreme conditions [27–30]. The PDs based on MoSe₂ nanoflowers showed the wonderful performance such as the impressive responsivity and rapid response time at zero bias with long-term stability and repeatability under simulated sunlight exposure in KOH electrolyte solution. Accordingly, it also provides some references for the exploration of MoSe₂ in the future.

2 Experimental section

2.1 Synthesis of MoSe₂ nanoflower

MoSe₂ nanoflowers were synthesized by the following procedure: the Se powers (99.9%, 0.316 g, Aladdin) with 10 ml Hydrazine hydrate (80 wt.%, Hunan Hui Hong Reagent Co., Ltd.) and Sodium molybdate dihydrate (99.8%, 0.484 g, Shanghai Macklin Biochemical Co., Ltd.) dissolved in a 100 ml beaker and then added a mixture of ethanol and water mixture of deionized water (10 ml) and alcohol (15 ml) under continuous agitation. The mixed solution was then moved to a 50 ml polytetrafluoroethylene lined stainless steel autoclave. The autoclave was sealed and kept at 200 °C for 24 h. The prepared black precipitates were collected with a 50 ml centrifuge tube and then centrifuged with ethanol for at least three times followed by drying at 60 °C for 10 h in vacuum. Finally, the centrifuged products were annealed in a Chemical Vapor Deposition (CVD) tubular furnace at 600 °C for 2 h. The preparation process of MoSe₂ nanoflower is presented in Fig. 1.

2.2 Characterizations of MoSe₂ nanoflower

The X-ray diffraction (XRD) showed the characteristic peaks of MoSe₂ nanoflowers with Cu Kα radiation at a scanning rate of 1.5° min⁻¹, which is compatible with the standard peaks. Raman microscope (Renishaw, In Via) was employed further observed the crystal structure at room temperature. Moreover, the microstructures of MoSe₂ nanoflowers was viewed by the Scanning Electron Microscope (SEM, JEOL, JSM-6360). The UV–visible spectrum of MoSe₂ nanoflower was measurement by the UV–visible spectrophotometer (Shimadzu Corporation of Japan, UV-2550).

2.3 Photo-response performance measurement

The prepared materials were weighed 1 mg and put into a 5 ml small centrifuge tube. Then, 1 ml N-methyl-2-pyrroldione was added to ultrasonic until the mixture was uniform. Coating the dispersed
mixed solution onto indium-tin oxide (ITO) conductive glass as working electrode. The opposite electrode and reference electrode respectively chose Pt electrode and saturated calomel electrode. The three electrodes were immersed in KOH electrolyte solution. A 150 W xenon lamp (280 ~ 980 nm) was used as the light source. In addition, the photocurrent tested was recorded the electrochemistry workstation CHI660D (Chen Hua, China). Finally, we promised that all measurements were conducted under the same environmental conditions.

3 Results and discussion

In Fig. 2a, the XRD patterns of the prepared MoSe$_2$ samples were shown. It is evident that the peaks of MoSe$_2$ nanoflowers prepared mainly located at the [002], [004], [100], [103], [105], [008], [200], [203], [118] direction. These peaks are consistent with the standard MoSe$_2$ diffraction peaks. To further ensure the quality of MoSe$_2$ nanoflowers, Raman spectroscopy was used to test Raman spectra due to the Raman measurements is considered to be an effective method to analyze the microstructure of nanomaterials all the time [31]. As clearly seen in Fig. 2b, the prepared MoSe$_2$ nanoflower exhibits three characteristic peaks in the spectral range of 200–400 cm$^{-1}$, which are, respectively, assigned to out-of-plane $A_{1g}$, in-plane $E_{2g}^{1}$ and $B_{1g}^{1}$ Raman active modes. The three characteristic peaks located at 241.2, 288.1 and 355.6 cm$^{-1}$ that are consistent with previous reports [32, 33]. Fig. 2c illustrates the MoSe$_2$ nanoflower with the crystal structure of the top view. Based on the SEM image in Fig. 2d, the flower-like structure surrounded by nanosheets can be clearly seen. Subsequently, in the UV–Vis absorption spectrum, we found that the nanoflowers prepared had better absorption of visible light, which is shown in Fig. 3. Therefore, in the following measurements, we always tested under simulated sunlight.

Considering the light response characteristics is an essential factor for detector. To gain the photo-response properties of MoSe$_2$ nanoflowers, the responsivity switching behavior of the electrode coated ITO materials under simulated sunlight illumination was studied by using a photoelectrochemical (PEC) test system. The schematic diagram of optical response test is shown in Fig. 4a. The further mechanism diagram is shown in Fig. 4b. As can be seen, with MoSe$_2$ dripping onto ITO contact with the KOH electrolyte, electrons will immediately flow from the photoanode to the electrolyte, leaving a hole where the electrons will accumulate on the side near the electrolyte and form a space charge layer. As electrons move to dynamic equilibrium, a built-in electric field is created. When incident light hits the photoanode, corresponding electron-hole pairs are
generated. The internal electric field drives the electrons through the external circuit to the opposite electrode, and then through the platinum electrode to the electrolyte. Besides, the holes in the surface will combine with the hydroxide in the electrolyte to achieve exchange charge. The opposite electrode will carry out the rapid transfer of electrons and generate the photocurrent [34].

Generally, while low mobility of carriers in electrolyte results in the low responsivity of PEC-type photodetectors, its unique three electrode structure design is incomparable to other types of detectors. Especially, they can provide power with themselves without external power supply. In the following test process, evaluated the photo-response performance of the MoSe2 nanoflower-based photodetection device with simulated sunlight illumination using the system. In Fig. 4, the photocurrent signal conversion behavior at 0 V is competitive compared to the analogous TMDs with the photoelectrochemical measurements. Clearly, the photocurrent density showed a trend of near linear growth with different power intensities, which reached 0.47 $\mu$A cm$^{-2}$ at...
60 mW cm\(^{-2}\) and photocurrent intensity was up to a maximum of 1.74 lAc m\(^{-2}\) for incident light power 140 mW cm\(^{-2}\) at 0 V bias. This can be attributed to the accelerated separation of photogenerated carriers at higher power densities. Besides that, the flower-like structure increased active regions resulting more enough absorption of light and accelerating the efficiency of current transmission, which may be beneficial for the large photocurrent density. Notably, the photo-response at 0 V certified the MoSe\(_2\) nanoflower-based photodetector working normally without external bias. In addition, MoSe\(_2\) nanoflower-based photodetector exhibited a competitive performance such as the eximious responsivity and the rapid response time, compared with other PEC-type photodetectors (See Table 1 for details) [35–38].

Importantly, the responsivity \(R_h\) and the response time are the essential parameters for the photodetection device, which introduced to evaluate the functional relationship between photocurrent density and light power intensity. The \(R_h\) obtained used the formula: \(R_h = I/J_{\text{light}}\), where \(J_{\text{light}}\) presented the power density and \(I\) was the photocurrent density. Introducing rise time \(t_r\) and decay time \(t_d\) were used to assessment the photo-response behaviors of the device. The \(t_r\) and \(t_d\) were defined to delegate the time interval of the rising (falling) time from 10% (90%) to 90% (10%), which were 0.15 s and 0.1 s, respectively. The response and recovery time were much more competitive compared with other photodetectors (Table 1 shows the detailed data). As shown in Fig. 5a, the photocurrent density at 0 V bias was incisively illustrated. And the illustration in Fig. 5a shows a schematic diagram of the response time and the relaxation time, selected one cycle from 100 mW cm\(^{-2}\) light response at 0 V. The electrolyte concentration as an indispensable factor for the change of the photocurrent which must be consideration. The variation of photocurrent density at different concentrations can be intuitively seen in Fig. 5b. Moreover, for the light response at 0 V obtained in Fig. 5a, we have run further tests, and the results are shown in Fig. 5c. The photocurrent density slightly increased with the increase of the optical power. The near linear growth result which was in line with expectations due to the separation of electron-hole pairs and the current transmission are closely related to the power separation of electron-hole pairs and the current transmission are closely related to the power. Then, the relationship between the

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**Table 1** The performance comparison with other photodetection device

| Material                | Measurement type and condition | Wavelength (nm) | Responsivity \(\mu\text{A W}^{-1}\) | Photocurrent density at 0 V \(l\text{Ac m}^{-2}\) | Response time (s) | Reference |
|-------------------------|--------------------------------|----------------|---------------------------------|-----------------------------------|-----------------|-----------|
| GaN nanowires           | PEC, \(V = 0\) V               | 365            | 322.5                           | 12.9                              | 0.28            | [39]      |
| Te@Se nanotubes         | PEC, \(V = 0.6\) V, 0.5 M KOH | 365–700        | 98.8                            | 7.79                              | 0.52            | [35]      |
| BP nanosheets           | PEC, \(V = 0\) V, 0.1 M KOH   | 365–546        | 1.9–2.2                         | 265                               | 0.5             | [36]      |
| NiPS\(_3\) flakes       | PEC, \(V = 0\) V, 0.1 M KOH   | White          | 3.79                            | 724                               | 5.8             | [38]      |
| InSe nanosheets         | PEC, \(V = 0\) V, 0.2 M KOH   | White          | 4.9                             | 15.9                              | 5               | [1]       |
| MoSe\(_2\) nanoflower  | PEC, \(V = 0\) V, 0.2 M KOH   | White          | 12.39                           | 1.75                              | 0.15            | This work |

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\(\text{PEC}\) stands for photoelectrochemical.
Fig. 5  

a The photocurrent density within five cycles at zero potential under simulated sunlight and the illustration shows the response time. 
b The photocurrent density curves at different concentrations. 
c The photocurrent density curve at different power with 0.5 M KOH. 
d The photocurrent density and optical responsivity at different power. 
e The EIS map of different KOH electrolyte concentration (0.05 M, 0.1 M, 0.2 M, 0.5 M)
photocurrent density and the light response is shown in Fig. 5d. There is clear that the responsivity increased from 7.5 to 12.39 μA W⁻¹ at 0 V when the incident light power intensity increased from 60 to 140 mW cm⁻². Meanwhile, the increase of electrolyte concentration leads to the increase of photocurrent density from 0.1 to 0.5 M because a high concentration of electrolyte can provide a relatively large number of conducting ions, in accordance with the EIS map of Fig. 5e. However, the less conductive ions in the lower electrolyte concentration have little influence on the carrier flow[40]. On top of that, in order to better understand the optical response of the device at different bias and more intuitively understand the performance of the detector. We showed the LSV curves under light and dark conditions in Fig. 6a. And then, the photocurrent density at different bias is shown in Fig. 6b. Clearly, the photocurrent density reached 1.088 μA cm⁻² at 0 V and attained 19.23 μA cm⁻² at 1 V when the light power was 100 mW cm⁻². The change of photocurrent density from 0 to 1 V may be due to the large specific surface area of MoSe₂ nanoflower reduces the scattering of light and increases the refraction of light, which leads to the full absorption of light, which is also good for the increase of photocurrent. In addition, the large specific surface area and high light absorption are sufficient to achieve charge exchange between the holes of MoSe₂ surface with the OH⁻ (h⁺ + OH⁻ = OH⁻) in the electrolyte [41].

More importantly, stability as a basic parameter to measure the performance of photodetectors must be involved, which is a more comprehensive assessment for the performance of the device. Here, the cycle stability and time stability were examined in 0.5 M KOH electrolyte. In Fig. 7a, the LSV curve after 100 cycles did not decrease significantly compared with the initial one, which proved the great cycle stability of the detector. In addition, to measure the time stability of MoSe₂ nanoflower-based photodetectors at 0 V bias, the long-time stability of the test up to 1000 s is explained in Fig. 7b and the obvious NO/ OFF switching signals is shown in Fig. 7c after the test. After 1000 s of continuous operation, the photodetector demonstrated greater potential in long-term measurement as the photocurrent continues to increase. Finally, Fig. 7d shows the stability in two weeks. Obviously, although the photocurrent was slightly reduced, it still maintained the pretty performance. Generally, the excellent stability provides a solid foundation for the research of MoSe₂ nanoflower-based photodetector.

4 Conclusion

In summary, we have successfully prepared the MoSe₂ nanoflower by a two-step method and fabricated a photodetector based on MoSe₂ nanoflowers with decent performances. The Raman and XRD measurements illustrated the great crystallinity of the MoSe₂ nanoflower. It was applied PEC-type photodetector and showed a self-powered performance with KOH, such as the short photo-response time and
the high photocurrent density and outstanding responsivity at 0 V bias. In addition, the MoSe$_2$ nanoflower-based photodetectors gained excellent cycle stability and time stability in 0.5 M KOH electrolyte solution, respectively. This work provides an effective way to study MoSe$_2$ nanoflower-based PEC-type self-powered detectors.

**Acknowledgements**

This work was financially supported by the Open Fund based on innovation platform of Hunan colleges and universities (Grant No. 19K095), the Grants from National Natural Science Foundation of China (Grant No. 11874316), the Program for Changjiang Scholars and Innovation Research Team in University (IRT 17R91).

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Declarations**

**Conflict of interest** The manuscript has no conflicts of interest and all authors agree to the publication of the paper.

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