Layered transition metal chalcogenophosphate towards air-stable visible light photodetection

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Abstract. Two-dimensional (2D) multiple-element layered transition metal chalcogenophosphates (TMCPs) have received tremendous attention due to their excellent carrier mobility, and absorption coefficient, displaying great potential for optoelectronic applications. Here, the novel high-quality manganese nickel phosphorous sulfur (Mn0.24Ni0.76PS3) crystals are obtained by using chemical vapor transport (CVT) method. Further, thin flakes of Mn0.24Ni0.76PS3 are achieved and employed to prepare photodetectors. Impressively, the prepared photodetectors exhibit excellent photo-response in visible light region, such as on/off ratio, and response time, a responsivity up to 10.4 mA W-1 and a detectivity of $1.31 \times 10^8$ Jones, demonstrating great potential for future air-stable visible light photodetection.

1. Introduction
Two-dimensional (2D) materials have attracted extensive attention since the discovery of graphene by exfoliation of bulk graphite. A large number of novel 2D material systems have emerged in the past few decades, including black phosphorus (BP), transition metal dichalcogenides (TMDCs), transition metal chalcogenophosphates (TMCPs) etc., which have witnessed the success of 2D materials. [1, 2] Among these materials, multiple-element layered TMCPs (the general formula is MPX3, where M is the magnetic transition metal, P refers to phosphorus, and X presents S or Se) have become a rising star in many fields owing to their rich varieties, wide bandgap ranges, and various magnetism states. [3,4] Interestingly, the physical and chemical performances of TMCPs were drastically varied by changing the elements or element ratios, resulting in adjustable optical bandgaps from 1.3 eV to 3.5 eV and magnetic states. [5] Therefore, 2D TMCPs offered attractive prospects in spintronics, catalysis, sensors, etc., and considered to be a promising candidate for next-generation electronic equipment.

TMCPs as newly developed broad bandgap semiconductors, have been also proposed for photodetection applications. [6, 7] In 2017, Chu et al. [6] first reported a highly sensitive UV photodetector based on NiPS3, which exhibited extremely low dark current and response time. A high on/off ratio of 200 and photoresponsivity of 126 mA W-1 were achieved at room temperature, implying great potential in UV light photodetection. Subsequently, tremendous efforts were devoted to the development of photodetector in TMCPs with various compositions and structures. [8-10] Recently, the photoelectric properties of MnPSe3 were systematically investigated, because it was predicated that process high carrier mobility and large absorption coefficient. The photodetectors based on MnPSe3 flakes also exhibited excellent photo-response in the ultraviolet region, [10, 11] thus 2D TMCPs are expected as a powerful candidate for ultraviolet photodetection in the future. Although the 2D TMCPs are suggested a wide wavelength response from near-infrared (NIR) to UV region, few reports have demonstrated their photoelectric performance at visible light or even the NIR regions. Just recently,
Ramos et al. [12] revealed an ultra-broad spectral-response, and good environmental stability in FePS₃ flakes, indicating great application potential in optoelectronics, and providing a novel avenue for exploring exciting magneto-optical or spintronic effects. Therefore, the performance of TMPC-based photodetectors still has much room for improvement and richness.

In this work, we successfully prepared the novel high-quality crystals of Mn₀.₂₄Ni₀.₇₆PS₃ by the typical chemical vapor transport (CVT) method, and comprehensively investigated the photo-response of this novel TMCP in visible light regions. The as-prepared single crystal processed 1.8 eV optical bandgap, and the fabricated photodetector displayed high off/on ratio, fast response time and high air stability.

2. Experimental section

2.1 Material and device preparation
Single crystals of Mn₀.₂₄Ni₀.₇₆PS₃ were grown by using the CVT method. The high purity Mn, Ni, P and S powders were mixed with additional iodine and heated at 600 °C for 10 hours in an evacuated quartz tube. Then, the zone of original materials was increased to 670 °C, establishing a temperature difference of ~ 70 °C, and held for one week. The dark crystals were collected in the low temperature zone, when the reaction was completed. The as-grown Mn₀.₂₄Ni₀.₇₆PS₃ flakes were obtained on SiO₂/Si substrates by using mechanical exfoliation method. For the fabrication of FET devices, the substrates with sample flakes were spin-coated with photoresist and baked in an oven. The drain and the source contacts were defined using a homemade standard UV photolithography. Finally, the Cr/Au (8/30 nm) electrodes were deposited by an electron beam evaporator (EBE) as source-drain contacts.

2.2 Characterization
The crystal structures and phase purities of the obtained crystals were identified by using X-ray diffraction (XRD, PAN analytical X’pert Pro X-ray diffractometer). The microscopy and chemical composition information of the obtained single crystal were performed using scanning electron microscope (SEM, S-4800, Hitachi, Japan) and energy dispersive X-ray spectrometry (EDS), respectively. The morphology of thin flakes obtained by mechanical exfoliation was investigated by an optical microscope. All of the optoelectronic characteristics were collected in a probe station, which is directly connected to a semiconductor analyser.

![Figure 1](image_url) Figure 1 Structure and characterization of 2D MPS₃ (M = Mn or Ni). (a) Front view, (b) left view, and (c) top view of few layer MPS₃. (d) XRD pattern of the MnPS₃, NiPS₃, and Mn₀.₂₄Ni₀.₇₆PS₃ single crystals. (e) Optical image of the exfoliated Mn₀.₂₄Ni₀.₇₆PS₃ flakes on SiO₂/Si substrate.
3. Result and discussion

The crystal structures of MPS₃ (M = Ni or Mn) were displayed in Figure 1a-c, which can be viewed as the monoclinic structure of space group C2/m (No. 12) with c = 0.679 – 0.663 nm. [6, 13] The crystal structure is built by the stacking of sandwich-like MPS₃ slabs bonded by van der Waals interaction in Figure 1a and 1b. Each MPS₃ unit cell is consisted of octahedral sulfur skeleton filled with M²⁺ and P-P covalent patterns. Six S atoms surround one M²⁺ cation forming the honeycomb arrangement as displayed in top view of MPS₃ in Figure 1c. To investigate the purity and crystalline quality of the as-prepared single crystals, XRD patterns were displayed in Figure 1d. The XRD patterns of MnPS₃ and NiPS₃ single crystals exhibited distinct sharp diffraction peaks marked as (00l), which can be indexed into the standard MnPS₃ (PDF#33-0903) and NiPS₃ (PDF#33-0952) patterns, respectively.[14, 15] For Mn₀.₂₄Ni₀.₇₆PS₃ single crystals, the corresponding diffraction peaks were shifted at a small angle and appeared in middle of MnPS₃ and NiPS₃, indicating the changed lattice parameters and the coexistence of Mn and Ni ions in the as-prepared crystals. Due to the low cleavage energy of Mn₀.₂₄Ni₀.₇₆PS₃ crystals, few-layered flakes can be achieved on SiO₂/Si substrates by using the typical scotch tape exfoliation method, as shown in Figure 1e.

Figure 2 showed the SEM images and various elements (Ni, Mn, P, and S elements) mapping images of the as-prepared single crystal. The bulk single crystal exhibits a flat surface with obvious layered steps and approximate hexagonal structure with an angle of ~ 120° in Figure 2a. The enlarged SEM image and corresponding element mapping images in Figure 2b-2f, showed a uniform distribution of various elements, indicating the uniform arrangement of Mn²⁺ and Ni²⁺ ions in the as-prepared single crystals. The elemental molar ratio of Mn:Ni:P:S was characterized by the EDS, corresponding to the stoichiometric ratio of Mn₀.₂₄Ni₀.₇₆PS₃, which is confirmed by the results of XRD.

Then, the as-prepared Mn₀.₂₄Ni₀.₇₆PS₃ flakes were exfoliated on the surface of SiO₂/Si substrates and fabricated to a two-electrode photodetector in Figure 3a. The optical bandgap of the as-prepared Mn₀.₂₄Ni₀.₇₆PS₃ crystals could be obtained by the UV-vis optical absorption spectrum in Figure 3b. The optical bandgap can be calculated by the following equation: [11]

\[
a \frac{hc}{k \lambda} = A \left( \frac{hc}{k \lambda} - E_g \right)^m,
\]

in which, \(a\) represents the absorption coefficient, \(h\) refers to the Plank constant, \(c\) is the propagation speed of light in vacuum, \(\lambda\) is the light wavelength, \(k\) is a constant of 1.6×10⁻¹⁹ J eV⁻¹, and \(m\) is 1/2 for

![Image](image_url)
direct bandgap. The direct optical bandgap of the as-grown single crystals can be confirmed as ~1.8 eV from the curve of \((\frac{ahc}{k\lambda})^2\) vs. \(\frac{hc}{k\lambda}\) in the inset of Figure 3b. Figure 3c displayed the \(I_{ds}-V_{ds}\) curves of the fabricated photodetector under dark condition and different wavelengths of visible light. The photodetector showed an ultra-low dark current \((I_{dark})\) (less than 1 pA under 5V bias voltage), implying a relative low stand-by power consumption. The prominent light responses of the fabricated photodetector were presented in the visible light range. The photodetector just been prepared, 1 day, 7 days, and 14 days later from its preparation. The photocurrents revealed a slight decrease with time, and reached ~75% of the original value after 14 days.

To systematically and quantitatively evaluate the optoelectronic properties, \(I_{ds}-V_{ds}\) curves of the prepared photodetector under several different wavelengths of visible light with various power intensity were measured in Figure 4a - 4c. The photodetectors based on Mn0.24Ni0.76PS3 flake presented a significant response under visible light, and displayed a trend of gradual increase with the increased light intensity. Figure 4d displayed the time-resolved photocurrent curves for switching incident 405 nm light with 98 mW cm\(^{-2}\) under a bias voltage of 5 V, indicating stability photocurrents. The response time of the fabricated photodetector is defined as the required time between 10 % and 90 % of the maximum photocurrent, as displayed in Figure 4e. The rising and decay times were calculated to be 3.22 ms and 3.10 ms respectively, which are one or two orders of magnitude shorter than the photodetectors based on other TMCPs. [11] To better evaluate the optoelectrical properties of the fabricated photodetectors based on Mn0.24Ni0.76PS3 flake, the responsivity (R) and specific detectivity (D*) were calculated by the formulae:

\[ R = \frac{I_{ph}}{PS} \]
\[ D* = R \frac{S^{1/2}}{2eI_{dark}^{1/2}} \]

where, \(I_{ph}, I_{dark}, S,\) and \(P\) refers to the photocurrent, dark current, effective area, and light power density, respectively. Figure 4f displayed the light intensity dependence responsivity and specific detectivity, the
maximum responsivity and specific detectivity were calculated to be 10.4 mA/W and $1.31 \times 10^8$ Jones under a 0.6 mW cm$^{-2}$ power intensity, respectively, which was attributed to the contribution of photoconductive effect. The responsivity can catch up with some photodetectors based on 2D TMCPs including CuInP$_2$S$_6$ (10.8 mA W$^{-1}$ @ 280 nm). [16] Although the responsivity was inferior to some photodetectors based on NiPS$_3$ (0.126 A W$^{-1}$ @ 254 nm), [6] MnPS$_3$ (288 A W$^{-1}$ @ 365 nm), [8] MnPSe$_3$ (22.7 A W$^{-1}$ @ 300 nm), [11] etc., the wavelength of light response was extended to 650 nm, which filled the gap of 2D TMCPs in the field of visible light detection. It is worth noting that the maximum responsivity and detectivity were appear at extremely low light intensity and high bias voltage as shown in Figure 4f. At low light intensity, the surface states of Mn$_{0.24}$Ni$_{0.76}$PS$_3$ flake was occupied by the photo-induced electrons, lead to a high carrier separation efficiency. The photo-generated electrons will quickly occupy the surface trap states until the trap states are completely occupied when the light intensity is increased. After that, the photo-generated electrons and holes will recombine immediately and not participate in the charge transfer process, resulting in a decreased R and $D^*$. [11]

4. Conclusion
In conclusion, the high-quality Mn$_{0.24}$Ni$_{0.76}$PS$_3$ single crystals were prepared by using the CVT method. The as-prepared single crystals presented good crystallinity, and a small band gap of ~ 1.8 eV. Moreover, the optoelectrical properties of the exfoliated Mn$_{0.24}$Ni$_{0.76}$PS$_3$ flakes were systematically studied. The photodetectors based on the as-grown Mn$_{0.24}$Ni$_{0.76}$PS$_3$ flakes presented excellent properties and air-stability in the visible light range with high responsivity of 10.4 mA W$^{-1}$, high on/off ratio and detectivity of $1.31 \times 10^8$ Jones, presenting great potential for the next-generation optoelectronics.

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