Metal halide-based photodetector using one-dimensional MAPbI$_3$ micro rods

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Abstract
In the present work, we report the fabrication of a photodetector using methylammonium lead iodide perovskite (MAPbI$_3$) micro rod. Photosensitivity of the Ag/MAPbI$_3$/Ag photodetector has been studied under various light intensities ranging from 10 to 100 mW/cm$^2$. The MAPbI$_3$ perovskite micro rod-based photodetector shows a high on/off ratio ($4.47 \times 10^5$), and fast response & recovery times (2.7 ms, each), as compared to the photodetectors using perovskite films. This work could initiate new perspectives for perovskite micro rods to be employed in high-performance optoelectronic devices.

1 Introduction
Photodetectors refer to optoelectronic devices that can convert incident light into electrical signals, are significant functional elements in a variety of areas such as environmental monitoring, fire deduction, and security, optical communications, space exploration, and video imaging [1, 2]. Different classes of semiconductor materials have been employed in photodetectors, such as GaN, InGaAs, Si, ZnO, carbon nanotubes, conjugated polymers, and quantum dots [3]. Devices based on these materials require complex and expensive manufacturing cost and mechanical inflexibility.

During the last decade, metal halide perovskite materials acquired a great interest of researchers due to their broad applications in photovoltaic and optoelectronic devices [4]. This class of material has been emerged as a potential candidate towards the future of plenty of photovoltaic and optoelectronic devices due to its outstanding high performance, low cost, and solution processability [5]. Among numerous available metal halides, methylammonium lead iodide (MAPbI$_3$) has been widely investigated for photovoltaic and photo-sensing applications [6].

Indeed, perovskite materials have achieved remarkable efficiency in photovoltaic devices, but these solar cells suffering long-term stability issues. Since the photodetector applications don’t require high power conversion efficiency and focus is instead given on the sensitivity of the device, cost-effectiveness, and ease of fabrication as compared to their counterparts, including Si or InGaAs based predominant photodetectors [7, 8]. Further, perovskite materials offer extraordinary features such as high charge carrier mobilities [9], light absorption over a broad spectral range [10], high absorption coefficient, flexibility, and low cost [11]. These characteristics consider perovskite material as a favorable contender for highly efficient photodetectors.

Many reports were published by numerous research groups based on the employment of perovskites as fast and highly sensitive photodetectors, revealing a broad spectral behavior from ultraviolet (UV) to visible (vis) wavelength range [12–14]. For example, Dong et al. [15] fabricated solution-processed broadband MAPbI$_3$ perovskite-based photodetectors and demonstrated fast response speed and high responsivity. Zhao and co-workers made organometal halide perovskite thin films on top of interdigitated (IDT) patterned gold (Au) electrodes and demonstrated highly sensitive and fast response speed photodetectors [16].

MAPbI$_3$ can attain either thin-film or crystal form; however, the perovskite crystals demonstrate far better behavior than the crystalline thin films [17, 18]. Moreover, nano- and micro-structured MAPbI$_3$ are more beneficial for optoelectronic applications due to their tunable optical bandgap, absorption coefficient, and carrier diffusion length [19]. The optical and electronic properties of perovskite crystals can be further tuned depending upon crystal structures (confined structure of lower dimensions...
Perovskite halides can form three-dimensional (3-D), two-dimensional (2-D), one-dimensional (1-D), or zero-dimensional (0-D) networks with the same unit structure [21]. Therefore, they can be employed innovatively to overcome conventional semiconductors pitfalls [22, 23]. Particularly, MAPbI₃ 1-D crystals offer a variety of attractive features such as length in the range of 3–4 mm, fewer heterostructure defects, and growth from simple solution-based technique [24]. Indeed, well defined MAPbI₃ crystal structures provide precise information about phase purity, connectivity between atoms, the surface to volume ratio, light absorption, etc. Randomly distributed perovskite crystalline structures result in deteriorated device performance [25]. Hence, consistent regular distribution and alignment of the crystalline structures make them more appropriate for the wavelength-specific photodetectors application [26].

The extensive use of perovskite wires in photodetectors, employing different fabrication techniques, has been reported in recent years. Horváth et al. [27] have fabricated MAPbI₃ nanowires-based photodetectors by a low-temperature solution processing slip-coating technique. In their work, they have made a comparison between the devices fabricated from nanowires and spin-coated films and have demonstrated distinct features of nanowires-based devices. Moreover, Deng et al. [18] have prepared high-performance photodetectors using perovskite small-diameter nanowires synthesized by a template method for control growth distributions of the monolayer. In the present work, the MAPbI₃ 1-D micro rods have been successfully employed to fabricate the photodetector. The facile solution processing technique is used to grow 1-D micro rods of MAPbI₃ perovskite, and their morphological and structural properties have been investigated as well.

### 2 Materials and methods

Lead (II) iodide (PbI₂) and methylammonium iodide (MAI) were purchased from Sigma-Aldrich and TCI Chemicals (Japan), while the Dimethylformamide DMF (anhydrous, 99.8%) and isopropanol (IPA) were obtained by Agros chemicals and VWR Prolab chemicals, respectively. All the chemicals were used as received. 1 M solutions of each PbI₂ and MAI were prepared in DMF and IPA, separately. The solutions were mixed in the 2:1 volumetric ratio to make the MAPbI₃ solution. Initially, the thick precipitates of perovskite were formed; however, simultaneous stirring and heating at 400 rpm and 70 °C produced a clear yellow MAPbI₃ solution. The resultant MAPbI₃ solution was allowed to cool down to the room temperature, at a prolonged rate (~ 10 °C/h), to form MAPbI₃ micro rods. The length of micro rods seems to increase within the solution in the vibration-free environment. Figure 1a demonstrates the stepwise synthesis of one-dimensional MAPbI₃ micro rods.

Commercially available pre-patterned interdigitated ITO/glass substrates (S161) were purchased from Ossila. The thickness of ITO on the glass substrate was 100 nm. Each substrate with dimensions (20 mm x 15 mm) (see the ITO/glass substrate image in the supplementary data file) consists of the five ITO based interdigitated sensation electrodes, while the each interdigitated sensation electrode consists of three channels with a dimension of 30 mm x 50 µm. An individual MAPbI₃ rod was placed over the pre-patterned ITO coated substrates. The two ends of the rod were fixed using silver (Ag) paste to produce Ag/MAPbI₃/Ag photodetector. Figure 1b shows the device structure of one-dimensional MAPbI₃ microrod based Ag/MAPbI₃/Ag photodetector. The surface morphology of the micro rods was performed using a field emission scanning electron microscope (FESEM). I–V characterization of the prepared device was recorded under different light intensities (10–100 mW/cm²) using an Oriel.

![Fig. 1](image_url)

Fig. 1  a A stepwise synthesis procedure for the preparation of MAPbI₃ micro rods. b Device structure of MAPbI₃ microrod based photodetector
AAA solar simulator (Newport) and a Keithley 2400 source measuring unit (SMU).

3 Results and discussion

Figure 2 shows field emission scanning electron microscope (FESEM) images of MAPbI3 micro rods at different magnifications. The FESEM micrographs exhibit the porous structure of MAPbI3 microcrystalline rods with an approximate diameter of ~60 nm while the length of the rod was 4-5 mm as described in our previous publication [24]. At higher magnification, the FESEM images reveal a well-aligned parallel arrangement of the perovskite submicron level crystals in the longitudinal direction. During the growth route, the crystals are joined in such a fashion that hollow regions are created. However, no adjacent cracks are visualized.

The elemental composition of the micro rods was studied using EDS analysis. The results in Fig. 3 show the existence of Pb and I as major components. The two featured peaks at 2.32, and 10.5 keV corresponds to lead, while the peaks at 3.98 and 4.2 keV belong to iodine elements in MAPbI3 crystals. In the case of MAPbI3, the atomic composition of microcrystals demonstrates the presence of MAPbI3 with I in the ratio of 1:2.1, which is consistent with MAPbI3, confirming the formation of pure phases.

The photodetector (PD), shown in the schematic device structure of Fig. 1b, is fabricated using a one-dimensional perovskite microrod. The photoresponse measurements were performed in the dark and under light illumination at intensities between 10 and 100 mWcm\(^{-2}\). The perovskite microrod absorbs incident photons with sufficient energy to generate excitons. Due to the applied and built-in electric field, the excitons are dissociated into electron-hole pairs (EHPs). The EHPs are, then, drifted to respective electrodes, which produce photo-generated current in the external circuit. Figure 4 shows current-voltage (I-V) characteristics of perovskite microrod based photodetector under multiple light intensities. The device responds well towards the incident light, even at low intensity of

![Fig. 2 FESEM images of the MAPbI3 micro rods at various magnifications](image-url)
incident light (~ 10 mW cm$^{-2}$), a noteworthy increase in the photocurrent is observed. The magnitude of photocurrent depends upon the generation of EHPs, which is directly correlated with the intensity of incident light, the greater the intensity, the greater the photocurrent. The photocurrent $I_{\text{light}}$ follows a power-law relationship with the intensity of incident light $P$ according to the following equation [28].

$$I_{\text{light}} \alpha P^\theta$$  \hspace{1cm} (1)

where $P$ is the light intensity, and $\theta$ is photocurrent response. When light strikes on PD, the EHPs are generated and swept to the corresponding electrodes producing photocurrent even at zero bias. A considerable increase in the photocurrent of MAPbI$_3$ with increasing light intensities is observed in Fig. 4. The light to the dark current ratio ($I_{\text{light}}/I_d$) of the PD at 0.5 V operational bias has been calculated as 4.49 ± 0.02 × 10$^5$. It is noteworthy that MAPbI$_3$ microrod based photodetector achieved an on-off ratio of about 10$^5$ that can be attributed to high carrier mobilities of holes and electrons [29]. The results, further, indicate that the EHPs are easily generated in MAPbI$_3$ microrod based PD under the influence of applied electric field between the electrodes.

Figure 5 reveals that the sensitivity of photocurrent is highly dependent on the operational bias voltage. A linear increase in the output current corresponding to the rise in

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**Table 1**

| El | An | Series | Unn. C [wt. %] | Norm. C [wt. %] | Atom. C [wt. %] | Error (1 Sigma) [wt. %] |
|----|----|--------|----------------|----------------|-----------------|----------------------|
| C  | 6  | K-series | 0.40          | 0.42           | 5.07            | 0.23                |
| I  | 53 | L-series | 54.80         | 58.64          | 66.50           | 1.70                |
| Pb | 82 | M-series | 38.25         | 40.94          | 28.43           | 1.44                |
| Total: | | | 93.45 | 100.00 | 100.00 | |
the externally applied potential can be observed from the Figure. At lower illumination intensities, the lines of applied potential tend to overlap; however, at higher intensities, the current for the applied potential varies significantly [30].

Inset, given in Figure 5, shows the response of open-circuit voltage $V_{oc}$ as a function of light intensities. The Figure demonstrates a linear increase in open-circuit voltage towards increasing light intensities. The voltage-dependent sensitivity $S$ of the device can be calculated by the following equation [31]

$$ S = \frac{I_{light} d}{PAV} \tag{2} $$

where $I_{light}$ is the illuminated current value, $d$ is the thickness of the rod, $P$ represents the power of incident light, $A$ defines the area of the rod, and $V$ is the applied bias. Similarly, the responsivity $R$ can be calculated using the equation given below [18, 30]:

$$ R = \frac{J_p}{P_{in}} \tag{3} $$

In this case, $J_p$ represents photocurrent density which can be further defined as $J_p = J_{light} - J_{dark}$ while the power of the incident light is represented by $P_{in}$. The sensitivity and responsivity were calculated as $8.67 \times 10^{-5}$ Sm/W and 0.76 AW$^{-1}$, respectively. The responsivity of the MAPbI$_3$ microrod based PD is compared with that of the MAPbI$_3$ film and microwires in Table 1. It is observed that the microrod, used in this work, exhibits better responsivity as compared to microwires.

The light-dependent switching (on and off) response (at an external bias voltage of 0.4 V and 100 mW cm$^{-2}$ illumination intensity) is presented in Fig. 6. The calculated response and recovery times were found as 2.7 ms, each. Our device exhibited superior performance in terms of on/off ratio and response time, as shown in Table 1. The on/off ratio of our device is $4.47 \times 10^5$, which is almost 100 times higher than the previous report on microwires [17]. Similarly, our device exhibited a response time of 2.7 ms, much faster than the thin-film based device, which is 200 ms [32].

4 Conclusion

In summary, one-dimensional MAPbI$_3$ micro rods were successfully fabricated to prepare the Ag/MAPbI$_3$/Ag photodetector, and their morphology was studied using FESEM. MAPbI$_3$ microrod based photodetector revealed outstanding performance in terms of sensitivity $(8.67 \times 10^{-5}$ Sm/W), on/off ratio $(4.47 + 0.02 \times 10^5)$, and responsivity $(0.76$ AW$^{-1})$. Moreover, the photodetector exhibited a fast response and recovery time of ~2.7 ms each. The results show that the perovskite micro rods can be potentially implemented to fabricate sensitive and rapid photoelectric switches and photodetectors.
Fig. 6  Response and recovery times of Ag/MAbI3/Ag photodetector

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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