High-performance perovskite photodetectors based on CH$_3$NH$_3$PbBr$_3$ quantum dot/TiO$_2$ heterojunction

Rajeev Ray$^{1,2}$, Nagaraju Nakka$^{1,2}$ and Suman Kalyan Pal$^{1,2}$

$^1$Advanced Materials Research Centre, India Institute of Technology Mandi, Kamand, Mandi-175005, Himachal Pradesh, India
$^2$School of Basic Sciences, India Institute of Technology Mandi, Kamand, Mandi-175005, Himachal Pradesh, India

E-mail: suman@iitmandi.ac.in

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Abstract
Organo-lead halide perovskite materials have opened up a great opportunity to develop high performance photodetectors because of their superior optoelectronic properties. The main issue with perovskite-only photodetector is severe carrier recombination. Integration of perovskite with high-conductive materials such as graphene or transition metal sulfi des certainly improved the photoresponsivity. However, achieving high overall performance remains a challenge. Here, an improved photodetector is constructed by perovskite quantum dots (QDs) and atomic layer deposited ultrathin TiO$_2$ fi ms. The designed CH$_3$NH$_3$PbBr$_3$ QD/TiO$_2$ bilayer device displays inclusive performance with on/off ratio of 6.3 $\times$ 10$^2$, responsivity of 85 A W$^{-1}$, and rise/decay time of 0.09/0.11 s. Furthermore, we demonstrate that interface plays a crucial role in determining the device current and enhance the overall performance of heterostructure photodetector through interface engineering. We believe that this work can provide a strategy to accelerate development of high-performance solution-processed perovskite photodetectors.

Supplementary material for this article is available online

Keywords: perovskite quantum dots, MAPbBr$_3$, heterojunctions, TiO$_2$, photodetectors

(Some fi gures may appear in colour only in the online journal)

Introduction

Photodetectors are sensors having widespread applications in optical communications, imaging, and chemical/biological sensing [1, 2]. At present, photodetectors made of inorganic semiconductors are ruling the markets [3–5]. The main disadvantages of these materials are non-flexibility, high processing cost and not environment-friendly, therefore, an alternative material could be a boon to the electronic industry [6, 7]. Organic–inorganic halide perovskites are serious contenders for next-generation photovoltaic technology [8–10] owing to their extraordinary optoelectronic properties such as direct bandgap, high absorption coefficients, low non-radiative Auger recombination, small exciton binding energies and, long lifetime and high mobility of photocarriers [9, 11, 12]. Within a very short period (about ten years) the power conversion efficiency of perovskite photovoltaic cells has reached 23.7% from 3.81% [13].

Recently, solution-processed perovskite-based photodetectors have shown great potential in photodetection [14–16]. Yang and co-workers reported a vertical perovskite photodetector [14] that exhibits excellent light-detecting capability. However, lateral photodetectors are easy to fabricate because of quite a simple device structure; their intrinsic gain mechanism can lead to very high photosensitivity [17]. The single-layer (lateral) perovskite photodetectors show relatively high detectivity ($\approx$10$^{12}$ Jones) and short response time (tens of milliseconds), but, low on/off ratio and poor electrical instability (induced by ion migration) [15, 18–20]. The photocurrent in single-layer perovskite photodetector
devices is relatively low because of fast recombination of the photogenerated carriers. These shortcomings are overcome in bilayer devices where perovskite, responsible for light absorption is placed on another material that transports charges. The carrier transport layer underneath the perovskite layer reduces recombination through efficient charge separation at the interface. Significant enhancement of photoresponsivity has been achieved in heterojunctions of perovskite and 2D materials such as graphene, MoS$_2$ [21], and WS$_2$ [22–28]. Graphene-based photodetectors [19, 23, 25, 26, 28] offer very low on/off ratio, whereas detectors with MoS$_2$ possess low rise and decay times [22, 24]. CH$_3$NH$_3$PbBr$_3$ nanoparticles (NPs) embedded in a mesoporous nanowire (NW) template not only exhibit strong cathodoluminescence, and photoluminescence but also show a high responsivity while used in a photodetector [29].

Perovskite quantum dot (QD) based photodetectors are being quickly developed as well. Wang et al [16] fabricated bilayer photodetectors with all-inorganic perovskite QDs and mesoporous TiO$_2$. Epitaxially blended CH$_3$NH$_3$PbBr$_3$ (MAPbBr$_3$) QDs and ternary PbS$_x$Se$_{1-x}$ QDs have been used as active layer in photodetectors [30]. However, the performance of perovskite QD based photodetectors is limited by low photoresponsivity. The performance of the perovskite QD based photodetectors can be enhanced through different approaches such as formation of heterojunction [31] and use of metal nanoparticles as hole transporting layer [32]. In this article, we have fabricated MAPbBr$_3$QD/TiO$_2$ heterojunction on fluorine-doped tin oxide (FTO) substrate for photodetection. Mesoporous TiO$_2$ films have been prepared via atomic layer deposition (ALD) technique for better transport of photocarriers. The fabricated bilayer devices exhibit excellent performance in terms of photoresponsivity and response time. The performance of the photodetector is found to be highly dependent on the quality of the perovskite/TiO$_2$ interface. But, UV-ozone treatment of the TiO$_2$ layer improves the detector performance.

Results and discussion

Characterization of MAPbBr$_3$ QDs and TiO$_2$ thin film

We prepared MAPbBr$_3$ QDs using facile solution process, which is given in the Experimental section. The transmission electron microscopy (TEM) image of perovskite QDs is illustrated in figure 1(a). It is seen from the inset of figure 1(a) that the size of QDs is ~6 nm. Additionally, the HRTEM image of QDs reveals an interplanar distance of 0.36 nm, suggesting the crystalline nature of the QDs (figure S1, available online at stacks.iop.org/NANO/32/085201/mmedia). Figure 1(b) depicts the x-ray diffraction (XRD) spectrum of the perovskite film. All the peaks (at 14.9°, 23.8°, 31.2°, and 46.04°) observed in the XRD spectrum are well matched to the tetragonal

![Figure 1](https://example.com/figure1.jpg)

(a) TEM image of MAPbBr$_3$ QDs. The inset shows the particle size distribution of MAPbBr$_3$ QDs. The size distribution of QDs is uniform with an average value 6 nm. (b) XRD spectrum of MAPbBr$_3$QD film. (c) Absorption and PL spectra of MAPbBr$_3$QD films. (d) XRD pattern of TiO$_2$ thin film prepared through ALD.

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Figure 1. (a) TEM image of MAPbBr$_3$ QDs. The inset shows the particle size distribution of MAPbBr$_3$ QDs. The size distribution of QDs is uniform with an average value 6 nm. (b) XRD spectrum of MAPbBr$_3$QD film. (c) Absorption and PL spectra of MAPbBr$_3$QD films. (d) XRD pattern of TiO$_2$ thin film prepared through ALD.
perovskite structure. No impurity peaks are observed other than those attributed to MAPbBr3. The morphology of the perovskite QDs film on the TiO2 layer is investigated using SEM. The SEM image in figure S2(a) suggests that QDs form uniform film. The thickness of the perovskite QDs film is around 250 nm (figure S2(b)). The light absorption spectrum of MAPbBr3 QD film is shown in figure 1(c). QDs exhibit strong absorption in the UV and visible light range with a peak at 490 nm. A strong photoluminescence (PL) is emitted from QDs at 520 nm (figure 1(c)). The narrow FWHM of the PL band suggests uniform size distribution of QDs, which is also apparent from the TEM histogram (figure 1(a)). The absorption edge of mesoporous TiO2 was appeared at 388 nm (not shown) indicating bandgap energy of 3.2 eV. Figure 1(d) shows XRD pattern of ALD-TiO2 film (annealed). The presence of 2θ peaks at 25.27° and 48.01° validates the anatase phase formation in TiO2 films. The PL intensity of the perovskite film was measured at different temperature over a period of time to study the thermal stability of the material (figure S3). While the PL intensity is reduced by a small amount at 75 °C, it remains constant at room temperature for many days suggesting considerably good thermal stability the perovskite film.

**Single layer versus bilayer devices**

When MAPbBr3 QD/TiO2 heterojunction is used as the active material in photodetectors, the photoelectrical performance is significantly enhanced. Figure 2(a) presents the schematic device structure for MAPbBr3 QD/mesoporous TiO2 heterojunction photodetector on patterned FTO coated substrate. To demonstrate the superiority of heterojunction photodetectors, two devices: only TiO2 (PDR) and MAPbBr3 QD/TiO2 (PD1) were fabricated. The thickness of the TiO2 layer was 50 nm in both the devices. Figure 2(b) shows the symmetric waterfall type I–V characteristics of the photodetectors suggesting ohmic contact between TiO2 film and electrodes, which is essential for good photoconductor and photodetector devices [33]. The dark current for the heterojunction device PD1 (green spheres) is lower than the dark current of the device PDR (red spheres) because of the formation of a low-conductive depletion region at the perovskite/TiO2 heterojunction. The photocurrent of PD1 increases dramatically up to 0.3 μA (at 5 V), which is more than one order of magnitude higher than that of PDR (figure 2(b)). The low photocurrent in PDR can be explained from the fact that TiO2 absorbs less light in the visible region due to very high bandgap as mentioned before. On the other
In the bilayer device, many photocarriers are generated in the perovskite layer upon light illumination because of its strong absorption in the visible light range. As shown in figure 2(c), MAPbBr3/TiO2 heterojunction possesses type II band alignment that causes photogenerated electrons to transfer into the underlying TiO2 film by spatially separating them from photogenerated holes. The separation of photogenerated carriers via electron transfer can reduce carrier recombination leading to low PL from perovskite QDs. It is proved strongly from the PL quenching of perovskite QDs (figure 2(d)) that the recombination of electron–hole pairs in QD film is suppressed because of the electron transfer to TiO2 layer. Nonetheless, the PL decay kinetics of perovskite film in the absence and the presence of TiO2 layer were measured using time correlated single photon counting technique. The PL decay in CH3NH3PbBr3/TiO2 heterojunction film is faster than that of CH3NH3PbBr3 film suggesting shorter carrier lifetime in heterojunction film (figure S4). This observation further supports our claim of separation of photogenerated carriers (in perovskite film) via electron transfer to TiO2. The injection of electron into TiO2 can enhance the conductivity of the TiO2 layer, which is the key requirement for high-performance of heterojunction photodetectors.

MAPbBr3 QD/TiO2 heterojunction photodetectors

In addition to PD1, two more devices having thickness of TiO2 layers 30 nm (PD2) and 20 nm (PD3) were fabricated. Similar XRD pattern (figure 1(d)) of TiO2 films of varying thickness (50, 30 and 20 nm) infers that there was no crystallographic change of the TiO2 layer with the change of thickness. The photoresponses of all three devices are presented in figures 3(a)–(c). The device PD1 produces the highest photocurrent (6.5 × 10^-6 A), while the lowest photocurrent (4.4 × 10^-6 A) is obtained from PD3. The photocurrents of all the fabricated photodetectors are consistent and reproducible. The on/off ratio of the three devices PD1, PD2 and PD3 are found to be 5.54 × 10^2, 5.0 × 10^2 and 3.7 × 10^2, respectively.

The transient photocurrent behavior of a photodetector can be understood through the response (rise or decay) time, which is one of the essential performance parameters for photodetection. The rise time (T_r) is defined as the transition time of the photocurrent from 10% to 90% of the peak value, while the decay time (T_d) is the time taken to decrease the photocurrent from 90% to 10% of the peak value [34]. Transient photoresponse curves for all three devices are provided in figure S5 (supporting information). The response time of the fabricated devices is calculated and presented in table 1. Clearly, the response of our perovskite QD photodetectors is much faster than recently reported values [35–39].

Table 1. Performance parameters of heterojunction photodetectors (PD1, PD2 and PD3).

| Device | Rise time (s) | Decay time (s) | Responsivity (A W^-1) | On/Off ratio |
|--------|---------------|----------------|------------------------|--------------|
| PD1    | 0.14          | 0.14           | 65                     | 550          |
| PD2    | 0.20          | 0.15           | 54                     | 500          |
| PD3    | 0.23          | 0.15           | 45                     | 370          |

Figure 3. (a)–(c) On and off photo responsive cycles of three different heterojunction photodetectors. PD1 exhibits better on/off ratio than other two devices. (d)–(f) AFM images showing surface roughness of TiO2 films of different thicknesses (50, 30 and 20 nm). The surface roughness is lowest for PD1.
Another important photoelectric characteristic of a photodetector is the responsivity \( R \), which can be defined as electrical output per optical input \([40, 41]\).

\[
R = \frac{\Delta I}{PS}
\]

where \( \Delta I = I_{on} - I_{off} \), \( P \) is the power density of the incident light, and \( S \) is the effective area under light exposure. The responsivity is found to be 65, 54 and 45 A W\(^{-1}\) for PD1, PD2 and PD3 devices, respectively (table 1).

It is evident from table 1 that the overall performance of the bilayer photodetectors depends on thickness of the TiO\(_2\) layer and the device PD1 exhibits highest performance. The devices having low roughness not only exhibit high on-off ratio, but also show better responsivity, and faster rise/decay time. The rise time is found to be 0.14, 0.20 and 0.23 s for PD1, PD2 and PD3 devices, respectively. Usually surface roughness of ALD grown TiO\(_2\) film is thickness dependent \([42]\). The AFM images of TiO\(_2\) films having thicknesses 50, 30 and 20 nm are shown in figures 3(d)–(f).

The rms values of surface roughness of these films is 10, 18 and 22 nm, respectively. Clearly, surface roughness varies with the thickness of TiO\(_2\) film. Nonetheless, the quenching of PL intensity of MAPbBr\(_3\) QDs is more for TiO\(_2\) layer of 50 nm thickness (figure 2(d)) suggesting much efficient transfer of electrons to the TiO\(_2\) film of lowest roughness. The roughness induced surface traps at the interface hinder the electron injection from perovskite to TiO\(_2\) \([42]\).

Hence, the efficiency of the electron injection to TiO\(_2\) layer increases with reduction of roughness of the interface. The improved electron injection increases the electrical conductivity of the TiO\(_2\) layer and finally leads to highest photocurrent in the device having thickest TiO\(_2\) layer. The effect of interface roughness on the process of charge transfer is presented diagrammatically in scheme 1.

Effect of surface treatment on the performance of heterojunction photodetectors

The accumulation of hydrocarbons on the rough surface of the TiO\(_2\) layer could deteriorate the quality of the interface affecting the charge transfer across the interface \([43, 44]\). Several surface treatments such as compact or blocking layer \([45]\), scattering layer \([46]\), atomic doping \([47]\) of the TiO\(_2\) films have been testified to enhance solar cell efficiency by improving the interface quality. Treatment with TiCl\(_4\) has been applied quite often to increase the efficiency of solar cells and optoelectronic devices \([48, 49]\). However, TiCl\(_4\) is not stable at room temperature as it reacts with moisture present in the air to produce the harmful hydrochloric acid \([50]\). It is also observed that oxygen ion beam treatment is efficient than oxygen plasma treatment for improving solar cell performance \([51]\). The main drawback of both oxygen ion beam treatment and oxygen plasma treatment is the requirement of considerable capital investment. However, UV-ozone (O\(_3\)) treatment is an effective and economical surface treatment method \([52]\). To examine the effect UV-O\(_3\) treatment, we fabricated a photodetector with UV-O\(_3\) treated TiO\(_2\) layer (thickness 50 nm). The \(I-V\) characteristics of the device was measured and is presented in figure S6 (supporting information). Time-dependent photocurrent and transient photoresponse curves (measured at 5 V) for ozone untreated and treated photodetectors are presented in figures 4(a)–(c).

The treated device exhibits on/off ratio, responsivity and rise/decay time of 630, 85 W A\(^{-1}\) and 0.09/0.11 s, respectively (table 2). Undoubtedly, the perovskite QD/TiO\(_2\) device displays very high overall performance following the UV-ozone treatment of the TiO\(_2\) layer. Recent advancements on the perovskite-based heterojunction photodetectors is summarized in table S1 (supporting information). In comparison to the recent progress, our MAPbBr\(_3\) QD/TiO\(_2\) heterojunction photodetector has significant advantages over response time and photoresponsivity.
To understand the effect of UV-ozone treatment, x-ray photoemission spectroscopy (XPS) measurements have been performed for untreated and treated TiO$_2$ films. Figures 5(a) and (b) show the C1s peaks of TiO$_2$ films. The intensity of C1s peak at 284.8 eV is found to be reduced after UV-O$_3$ treatment. The quantitative analysis of peaks reveals that the area under C–C peak is decreased after UV-O$_3$ treatment. This observation suggests that UV-O$_3$ treatment burns out organic contaminants present on the surface of TiO$_2$ and thereby clean the surface of the film. The O1s peak at 530.1 eV (figures 5(c)–(d)) is associated with oxygen bonding to coordinatively saturated titanium atoms (lattice oxygen of TiO$_2$). The signal at higher binding energy (531.5 eV) could be attributed to the formation of Ti$^{3+}$ surface states through the creation of oxygen vacancies, which is normally inscribed as Ti$_2$O$_3$ [50]. The ratio between the numbers of oxygen atoms present was estimated by comparing areas under Ti$_2$O$_3$ peaks and found to be increase from 8.2% to 15.4% after the UV-O$_3$ treatment. Therefore, the change of oxidation state from Ti$^{4+}$ to Ti$^{3+}$ takes place through the introduction of negative oxygen species (O$^-$) on the surface of TiO$_2$ during treatment.

Table 2. Performance parameters of photodetectors before and after ozone treatment.

| Device          | Rise time (s) | Decay time (s) | Responsivity (A W$^{-1}$) | On/Off ratio |
|-----------------|---------------|----------------|----------------------------|--------------|
| Ozone untreated | 0.14          | 0.14           | 65                         | 550          |
| Ozone treated   | 0.09          | 0.11           | 85                         | 630          |

Figure 4. (a) Current versus time graph of UV-ozone treated and untreated photodetectors at 5 V. (b)–(c) Transient photocurrent response (rise/decay time) for ozone-treated and untreated photodetectors. Both on/off ratio and response time of the photodetector is improved following UV-ozone treatment.

Figure 5. XPS spectra of TiO$_2$ films on FTO glass substrates. (a), (c) Untreated and (b), (d) UV-ozone treated TiO$_2$ films. Gaussian/Lorentzian peak fitting technique is used to identify the contribution of individual species. The intensity of C1s peak at 284.8 eV decreases because of removal of hydrocarbons from the interface during UV-ozone treatment. The increased contribution of Ti$_2$O$_3$ peak (at 531.5 eV) in treated film suggests the formation of Ti$^{3+}$ surface states.
UV-O₃ exposure [44, 53, 55, 56]. Oxygen vacancies generated during the reduction of Ti⁴⁺ to Ti³⁺ produces electrons, which affect the surface functionality and charge state of the TiO₂ film.

The additional electrons generated by UV-O₃ treatment improve the carrier transport property of TiO₂ film resulting high photocurrent and fast response of the photodetectors. Nonetheless, because of less carbon contaminants, more perovskite QDs could be adsorbed on the TiO₂ surface by refining the quality of the heterojunction.

**Conclusions**

In summary, MAPbBr₃ QD/TiO₂ heterojunction photodetectors were fabricated using atomic layer deposited ultrathin TiO₂ films. Due to the improved conductivity of TiO₂ layer through the efficient extraction of electrons at the interface, the performance of heterojunction photodetectors is increased. The performance of such photodetectors depends on the interface quality and the device having lowest interface roughness offers highest performance. UV-ozone treatment of the TiO₂ layer enhances the device performance by improving both the interface quality and conductivity of the TiO₂ layer. The heterojunction device exhibits high responsivity of 85 A W⁻¹, and short rise/decay time of 0.09/0.11 s. In comparison to the reported perovskite-based heterojunction photodetectors, the MAPbBr₃ QD/TiO₂ device exhibits very high overall performance. Our findings could be beneficial to developing perovskite-based flexible heterojunction photodetectors.

**Experimental methods**

**Materials.** All chemicals were used without further purification. Lead (II) bromide (PbBr₂, 99%, Sigma Aldrich), methylamine (CH₃NH₂, Sigma Aldrich), hydrochloric acid (HCl, 37 wt% in water, Sigma Aldrich), hydrobromic acid (HBr, 48 wt% in water, Sigma Aldrich), oleic acid (Sigma Aldrich), N,N-dimethylformamide (Sigma Aldrich) were used for the preparation of perovskite QDs.

**Synthesis of MAPbBr₃ QDs.** Methylammonium bromide (CH₃NH₃Br) was prepared through a reaction of methylamine in ethanol with HBr at room temperature. HBr was added dropwise while stirring. Upon drying at 100 °C, a white powder of CH₃NH₃Br was formed. The powder was dried overnight in a vacuum oven and purified with ethanol. CH₃NH₃Br (32 mg) and PbBr₂ (92 mg) were dissolved in anhydrous dimethylformamide (DMF, 3 ml) with rigorous stirring at 50°C. Thereafter, oleic acid (0.4 ml) and oleylamine (0.2 ml) were added to the solution with continuous stirring at 60 °C. Then the precursor solution was added into 3 ml chloroform under rigorous stirring at 90 °C to obtain highly green luminescent perovskite QDs. The cleaning of the perovskites was done through centrifuge and stored in air tight glass vial for further use. It is noteworthy to mention that the colloidal solution of nanocrystals remains stable for few months.

**Device fabrication.** Photodetectors were fabricated on pre patterned FTO coated glass substrates (sheet resistivity 7 Ω cm⁻²) with a channel length of 5 μm and width of 2 μm. First, substrates were cleaned by ultrasonication in a soap solution, deionized water, acetone, and isopropanol, respectively. The cleaned FTO substrates were baked for 30 min before ozone treatment. Then, the ultra-thin layer of TiO₂ was deposited by ALD on FTO at 150 °C. The thickness of the TiO₂ films was controlled by varying the deposition cycles. Next, perovskite QD films were deposited on the TiO₂ layer by spin coating the QD solution at a speed of 700 rpm for 30 s. The fabricated devices were annealed at 100 °C to enhance the device performance by improving the quality of MAPbBr₃ QD/TiO₂ interface.

**Measurements.** Synthesized QDs were characterized by absorption and photoluminescence (PL) spectroscopy using Shimadzu UV-2450 spectrometer and Cary Eclipse spectrophotometer from Agilent Technologies, respectively. The dimension of the QDs was estimated from TEM using TECNAI G2 200 kV (FEI, Electron Optics) electron microscope. XRD was performed in a Smart Lab, RIGAKU 9 kW rotating anode diffractometer. The surface morphology and thickness of compact TiO₂ layer were characterized using atomic force microscopy (Dimension Icon from Bruker) in tapping mode at room temperature and ellipsometry (Accurion EP4), respectively. Current–voltage (I–V) characteristics and photodetection measurements were carried out using a class 3A solar simulator (OAI TriSOL) having light intensity 0.1 W cm⁻² and equipped with a Keithley 2400 source meter unit. We performed XPS in a SPECS instrument with a PHOIBOS 100/150 detector (DLD) at 385 W, 13.85 kV, 39.6 nA (sample current), and a pass energy of 50 eV. Curve synthesis and deconvolution, i.e. identifying the components of the XPS signals, were performed by fitting the XPS signal with Gaussian/Lorentzian function. The binding energies were calibrated using the C1s peak for adventitious carbon at a binding energy of 284.5 eV, with an associated error of ±0.1–0.2 eV. Scanning electron microscopy was performed through SEM, Nova Nano SEM-450, FEI.

To characterize thermal stability, we placed perovskite films on a hotplate and annealed at 80 °C for 240 h in a N₂-filled glovebox. After every 24 h the PL of the film was measured.

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