Facilitation Centre for Industrial Plasma Technologies
Institute for Plasma Research

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Rangoli made by FCIPT Staff during Diwali 2020

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Highlights

- All-inorganic Pb-free perovskite
- Extended absorption based on phonon-assisted transition
- Self-powered and broadband photodetection
- Long environmental stability under 75% relative humidity

Research Focus :

All-Inorganic Lead-Free Perovskite for Self-Powered Photodetector with Extended Spectral Response

Since the discovery of the state-of-the-art hybrid halide perovskites, their application in optoelectronic systems has drawn considerable attention. Research interest in halide perovskites has intensified in last few years since their debut in 2009.[1] Ever since, the progress of halide perovskites have been spurred by its unique chemical composition with a general crystal structure of ABX_3, where A and B are cations and X is a halide anion.[2] Based on the crystal structure, the halide perovskites emerge as a classic example where an apparently simple elemental configuration can give rise to a variety of interesting properties such as the tunable optical bandgap, strong absorption coefficient and long exciton diffusion length.[2] These specific properties of halide perovskites render them as excellent candidates for optoelectronic applications, such as solar cells,[1] photodetectors, light-emitting diodes (LEDs), lasers and so on.[2] Emphasizing on the optoelectronic applications, the scientific community has shown significant enthusiasm in studying these halide perovskites in the field of photodetectors.

However, it is worth to mention that most of the high performing perovskite photodetectors are based on organic-inorganic lead (Pb) containing constituents. Therefore, in spite of the glorious photo-responses of photodetectors, there remain numerous challenges in bringing this technology to future large-scale market. One major limitation is the use of Pb-component in the perovskite structure which increases the toxicity level. Simultaneously, the easy volatilization and hygroscopic nature of the organic cations (methylammonium (MA^+), formamidinium (FA^+), $CH_3(NH_2)_2$, NH_4^+ etc.) in the perovskites, continues to be a major concern towards the ambient stability of the photodetectors. In order to address these problems, the search for efficient Pb-free halide perovskites has begun. Various efforts have been made to substitute the Pb with tin (Sn),[3] antimony (Sb),[4] bismuth (Bi),[5] and copper (Cu).[6] Among these, Bi-based halide perovskites have gained significant attention with regards to its low toxicity and chemical/ambient stability.[7]

Specially highlighting the reported photodetectors based on all-inorganic caesium based perovskites, it is found that they always work under an applied operating voltage (1 – 30 V). Moreover, the utilized incident light intensity for light detection is high, typically within the range (0.2 – 100 $mWcm^{-2}$) with a considerably smaller device active area of 0.03 to 1.8×10^{-5} cm^2. Importantly, the wavelength selectivity is also narrow within 300 – 600 nm. Therefore, it is of extreme importance to produce cost-competitive photodetectors capable of detecting low optical signals and broad spectral range with a larger area for all practical applications. Besides, the benefit will become manifold if the photodetector can work under low/zero applied bias (self-powered mode) and can offer broadband photodetection. Hence, it is believed that the successful implementation of the mentioned issues will certainly improve the photodetector geometry thereby facilitating a compact and portable optoelectronic circuit.

In the present study, an effort has been made to fabricate all-inorganic Pb-free photodetector. Herein, a $Cs_3Bi_2I_9$ perovskite photodetector is demonstrated, being one of the few Cs-based Pb-free perovskite photodetectors reported till date.[8] Studies have been made in two important aspects: First, the synthesis of a robust $Cs_3Bi_2I_9$ perovskite film considering its individual structure-property relationship using a simple solution-based approach; Second, the construction of a self-powered photodetector using the as-synthesized $Cs_3Bi_2I_9$ perovskite employing a simple device architecture. Initially, the systematic investigation of the optical, structural and morphological features shows the strong absorption coefficient (2.6×10^4 cm^{-1}), good crystallinity and consistently grown micrometre-sized crystals of $Cs_3Bi_2I_9$ perovskite. An interesting feature is the existence of a weak absorption tail within 750 – 950 nm which is the characteristics of a phonon-assisted transition. Subsequently, the optoelectronic features of the photodetector are investigated in detail. An impressive photo-response is observed showing the existence of a clear self-powered operation (zero bias) with a significantly low dark current of 0.46 pA. Profiting from the self-powered operation and low dark current, high photosensitivity of 1.4×10^4 is estimated. Moreover, the appreciable responsivity (0.59 μAW^{-1}, 3.8 mAW^{-1}) and detectivity (1.2×10^{10}, 1.6×10^{12} Jones) values are estimated at zero and 1 V biases under a comparatively weak optical signal (0.1 $mWcm^{-2}$) and a larger device active area (0.25 cm^2). Additionally, the photodetector covers a broad spectral range (450 – 950 nm) at zero bias employing a simple device geometry without the use of any intermediate electron/selective layers or without modifying the perovskite by the inclusion of mixed halides and dopants. The photodetector also exhibits highly stable photo-switching with a rise time of 62.74 ms and a decay time of 90.25 ms at zero bias.

Additionally, the photodetector demonstrates excellent photo-stability and long-term stability of three months after exposure in the ambient environment (Figure 1). Furthermore, the performance of the as-fabricated photodetector is compared with the reported Cs-based Pb and Pb-free perovskite photodetectors which shows effective performance by balancing all the critical photodetection parameters (Table 1). It is noteworthy that, here the device architecture is intentionally not modified with respect to the earlier reports so that it can directly show the feasibility of the present perovskite photoresponse in a common vertical-type geometry. It will also allow to directly compare the response parameters with that of the earlier reports.

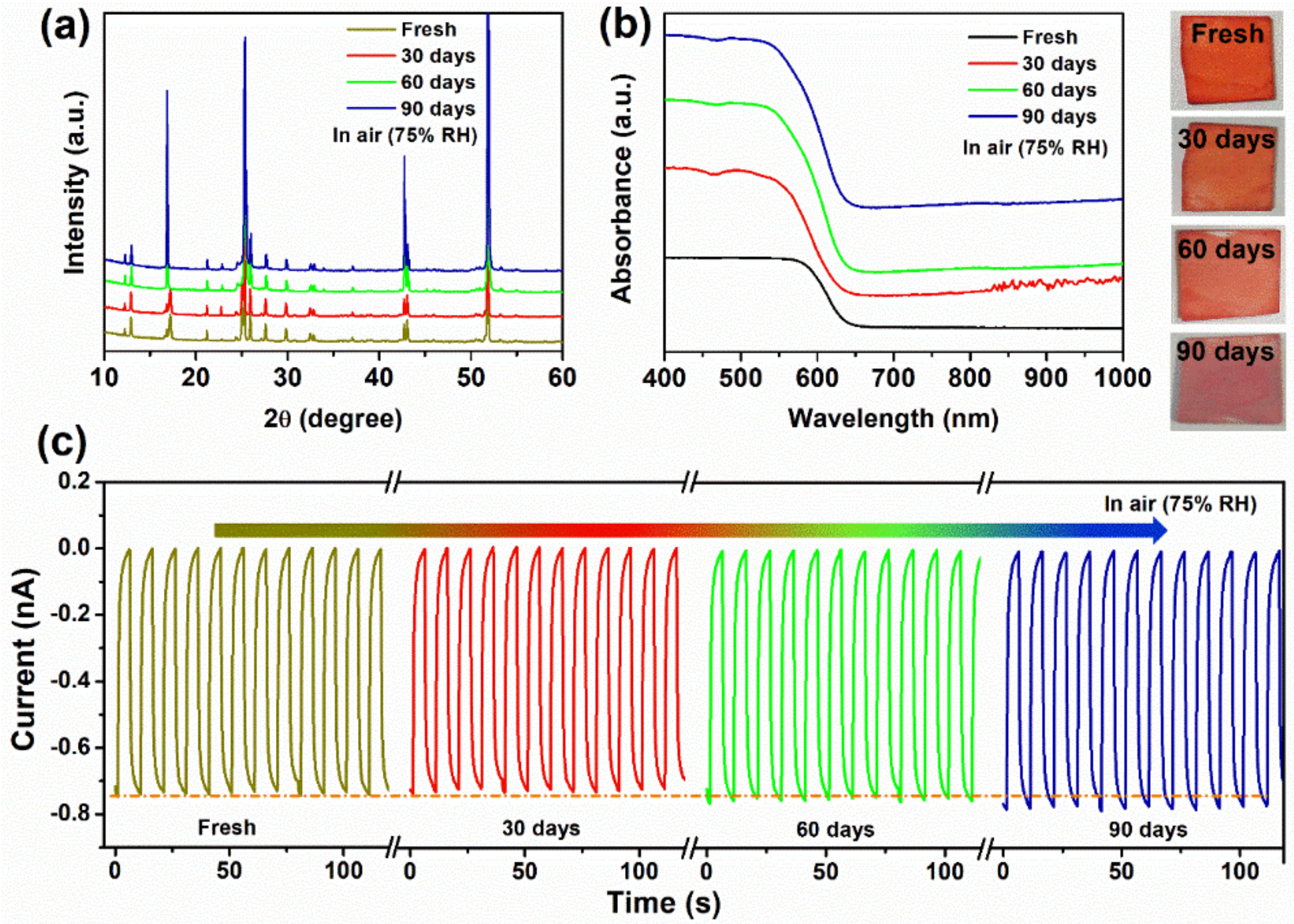

Figure 1. (a) XRD pattern (b) UV-visible absorbance spectra (along with the original photographs) of the fresh and the aged $Cs_3Bi_2I_9$ film after storage for 90 days. (c) Transient switching curve (I-t curve) of the photodetector under white light at 0.1 Hz frequency after storage for 90 days in air (75% RH).

Table 1. Performance comparison of the present $Cs_3Bi_2I_9$ halide perovskite photodetector with the other reported Cs-based Pb/Pb-free iodide perovskite photodetectors.

Active Material	**Opt. Volt. $^{(a)}$ (V)**	**$A^{(b)}$ (cm^2)**	**$l^{(c)}$ (nm)**	**$P_{in}^{(d)}$ ($mW\text{-}cm^{-2}$)**	**$R_l^{(e)}$ ($A\text{-}W^{-1}$)**	**$D^{*(f)}$ (Jones)**	**$\tau_r^{(g)}$ (s)**	**$\tau_d^{(h)}$ (s)**	**Ref.**
$Cs_3Bi_2I_9$	0	0.25	450 – 950	0.1	0.59 µ	1.20×10^{10}	62.74 m	90.25 m	Present-Work[8]
$Cs_3Bi_2I_9$	1	0.25	450 – 950	0.1	3.8 m	1.60×10^{12}	88.66 m	109.3 m	Present Work
Cs-based Pb-free iodide perovskite photodetectors									
$CsBi_3I_{10}$	1	6×10^{-4}	650	0.2	21.8	1.93×10^{13}	0.33 m	0.38 m	2017
$Cs_3Bi_2I_9$	10	-	450	1.21	33.1 m	$\sim 10^{10}$	10.2 m	37.2 m	2019
$Cs_3Bi_2I_9$ PC	-2	-	White Light	100	7.0 m	9.30×10^9	0.58 m	0.38 m	2020
$Cs_3Bi_2I_6Br_3$	0	0.0314	300 – 600	75	15 m	4.60×10^{11}	40.7 m	27.1 m	2020
Cs-based Pb iodide perovskite photodetectors									
$CsPbI_3$ NRs/ C8BTBT	-30	-	White Light	10	4300	-	~s	~s	2018
$CsPb_{0.922}Sn_{0.078}I_3$ NBs	2	-	405	1.96	1.18×10^3	6.43×10^{13}	240 m	271 m	2018
$CsPbI_3$ NWs	1	1.8×10^{-5}	530	5.485	0.35	1.64×10^{10}	~s	~s	2018
$CsPbI_3$ NWs	1	0.0314	White light	1.5	6.7 m	1.57×10^8	292 m	234 m	2017
$CsPbI_3$ QDs/ DPP-DTT	-30	1×10^{-3}	405	0.008	110	2.90×10^{13}	3.2	3.3	2018

(a) operating voltage; (b) effective illuminated area; (c) wavelength of light; (d) incident power density; (e) responsivity; (f) specific detectivity; (g) rise time; (h) decay time; NWs, nanowires; NRs, nanorods; NBs, nanobelts; PC, poly-crystal; QDs, quantum dots.

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Past Events

Technology Transfer

Know-how and License Agreement

A non-exclusive agreement of technology license was signed between Institute for Plasma Research, Gandhinagar; and M/s Ankur Scientific Energy Technology Pvt. Ltd., Vadodara; to dispose infectious biomedical waste using "Plasma Pyrolysis Technology". The agreement was signed on 30th Oct 2020, during the commemoration of 111th birth anniversary of Dr. Homi Jehangir Bhabha, father of Indian Atomic Energy programme. M/s Ankur Scientific is engaged in the business of biomass gasification and waste to energy technologies and has shown interest in commercializing the technology of plasma pyrolysis developed by FCIPT-IPR for Bio-Medical Waste disposal. IPR has provided know-how to M/s Ankur Scientific and will provide supportive scientific and technical assistance as per the agreement. This will enable M/s Ankur Scientific to effectively manufacture, market, supply and provide after sales support for plasma pyrolysis systems.

Officials of IPR and and M/s Ankur Scientific Energy Technology Pvt. Ltd., exchanging the agreement

Past Events

Inauguration of an Incubation Centre at IPR, on 30th Oct 2020

Director, Dr. Shashank Chaturvedi and other officers of IPR attending the online inauguration ceremony

On 30th Oct 2020, incubation centres at BARC Mumbai, IGCAR Kalpakkam, RRCAT Indore and IPR Gandhinagar were inaugurated by Shri. K.N. Vyas, Secretary Department of Atomic Energy (DAE) & Chairman Atomic Energy Commission. The inaugural ceremony was held online during the commemoration of the 111th birth anniversary of Dr. Homi Jehangir Bhabha, father of Indian Atomic Energy programme. This day is also observed every year as Founder's Day of Bhabha Atomic Research Centre (BARC), Mumbai. The establishment of the incubation centres is in line with finance minister Smt. Nirmala Sitharaman's May 2020 reform proposals.

In a brief introduction during the inaugural ceremony, Director IPR, Dr. Shashank Chaturvedi, spoke on the technologies developed by IPR. Facilitation Center for Industrial Plasma Technologies (FCIPT) was declared as the site where the incubation center would be located. A brief one minute video was also displayed, that exhibited many technologies developed by IPR such as plasma pyrolysis, plasma nitriding, plasma gasification, artificial intelligence for detection of medical conditions, to name a few. During this event an exchange of transfer of technology agreement of plasma pyrolysis technology on biomedical waste disposal was done between IPR and M/s Ankur, Vadodara.

The incubation centre will help entrepreneurs to absorb technologies developed by IPR for societal benefits. IPR will provide technical consultancy and basic infrastructure facility to develop more understanding of the developed technologies and will also give know-how of these technologies through technology transfer agreements. This was also made clear in the speech by Shri. K. N. Vyas where he mentioned that "The incubation centers will take DAE's already established technologies to the wider society through relevant products."

"Plasma for a safe future"

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