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Fabrication and study of structural, optical features of nano structured, photo-harvesting organo-lead halide-based perovskite solar cell

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Abstract

In a world where conventional sources of energy are fast depleting, the quest for alternative energy sources may hold the key for the survival of humanity. In the present work, emphasis has been given to the idea of producing energy from perovskite based solar cells. In order to bring this idea into fruition, a unique and novel nano structured perovskite material *n*-propyl ammonium lead chloride ($C_3H_7NH_3^+PbCl_3^-$) was prepared through a unique co-precipitation route using *n*-propyl amine (n-$C_3H_7NH_2$) and hydrochloric acid as the starting precursors with aqueous solution of $Pb(CH_3COO)_2 3H_2O$. Finally acetic acid was added to the solution and this solution was allowed to concentrate and then gradually cooled down to room temperature. After math, the synthesized material was spin-coated on TiO_2 film to fabricate the solar cell. The device was then undergone systematic analysis using XRD, SEM, UV and Photo Conversion to get a transparent idea regarding its structural, electrical and optical properties. When experimentally applied, this perovskite-based solar cell has shown energy conversion efficiency (η) of around 6.01 % which is noticeably good. Thus it can be concluded that this material is promising for fabrication of vastly efficient solar cells. This technology can be tried in large scale as an alternative of conventional energy in the near future.

Keywords: Perovskite materials; energy; band-gap; photo-efficiency.

Introduction

Keeping the exponential growth of world population in mind, it is only natural to predict that the demand for energy will only go up [1]. It can never be denied that energy is the key driving force for the advancement in human living standards and hence, in coming years the worldwide energy consumption is expected to be double [2,3]. Since 1991, Solar Cells have received much attention as a prime example of next generation photovoltaic devices [4-8]. As of now, the efficiency of dye-sensitized solar cells (DSSCs) and perovskite solar cells (PSCs) have reached ~20% of efficiency [9,10]. Although the performance of certain PSCs, fabricated by different groups with one-step techniques, has reached ∼18%–20% efficiency, it is normally ∼15%–16% for most laboratories because of the aforesaid reasons [11-14]. Despite of high efficiency in DSSC, the commercialization of the same has been hindered due to the chief issues related to instability-factor, leakage of liquid electrolytes etc. [15-19]. Consequently, DSSCs possessing organic hole transfer material (HTM) have drawn greater focus due to their stability [20] and comparable efficiency [21]. For hybrid perovskite solar cells, long-term stability may be attained in future works [22]. Besides the factor of higher efficiency, this stability factor is the key reason for scientists to concentrate on the fabrication of perovskite based solar cells. Perovskite layers with smooth surface morphology, large grain sizes are helpful to obtain higher efficiency [23,24]. As film non uniformity is reduced in large-area PSCs, modified surface planarity is required in order to minimize energy loss in weak links [25,26].

Presently nano structured semiconductor materials impregnated in solar cells are widely gone through due to their favorable performance as these materials can surge the absorption capability [27]. This nano phot -materials also have the benefit of stability due to their intrinsic dipole moments and high extinction co-efficient as well [28]. Besides, appropriate nano morphology can uplift the charge-carrier transport inside the participating layers of the material. Solar radiation is directly used to generate electricity in facile way to channelize the renewable energy flow via electrochemical devices [29,30]. It is also beneficial because power can be generated at the users' place. Different types of photovoltaic devices, such as thin film solar cells, crystalline silicone, semiconductor based solar cells, organic-inorganic hybrid (Perovskite) solar cells, DSSCs and bulk hetero junction solar cells are used world-wide [31,32]. Among all the devices, the PSCs and DSSCs have been regarded as potential contenders for power-generation. Organic sensitizers and solid electrolytes or HTM are the building unit of the DSSC and perovskite hybrid nano materials are the hearts of the PSCs [33].

A lot of working systems have been generated by using perovskite material methyl ammonium lead chloride as the basic unit of solar cell [33-35]. In one [3] of our previous works, we have used ethyl ammonium lead chloride effectively as the basic unit of perovskite solar cell. But there is no notable evidence of making solar cell using the perovskite material *n*-propyl ammonium lead chloride (n-$C_3H_7NH_3PbCl_3$). In the present work, we have synthesized nano structured *n*-propyl ammonium lead chloride deposited on TiO_2 film for fabrication of the solar cell. We have used SEM analysis in order to study the surface-morphology of the synthesized material. We have performed XRD to reveal the crystalinity of the synthesized material. UV-spectra and calculation of Photo conversion efficiencies were done to get a proper view regarding the optical and electrical properties of the cell respectively. Our synthesized photo-active, perovskite material is completely unique and novel as no previous references of this material have been found as per our literature-survey.

Materials and methods

Lead (II) acetate [$Pb(CH_3COO)_23H_2O$] purity 99.99%, hydrochloric acid (purity 99%) and *n*-propylamine (purity 99%) for the precursor solution of *n*-$C_3H_7NH_3PbCl_3$ were bought from Sigma-Aldrich, India. The components which had been used in the preparation of the TiO_2 sol-gel films are given below: Titanium isopropoxide (TIP) ($Ti[OCH(CH3)_2]_4$ purity 99%), ethanol (CH_3CH_2OH, purity 99.9%) and acetic acid (CH_3COOH, purity 99.5%). All these were purchased from Sigma-Aldrich, India. Glass slide coated with transparent, conducting fluorine doped tin oxide (FTO) was used as substrate.

Fabrication of perovskite solar cell

Sol-gel spin-coating method was used to prepare TiO_2 thin film. Firstly, a mixture of 5 ml of acetic acid solution and 50 ml of ethanol was stirred for 5 min in magnetic-stirrer. Then 6.8 ml of Titanium isopropoxide was added by pipette to the beaker containing the stirred mixture of acetic acid and ethanol. The mixture underwent continuous stirring and for a further two minutes after addition of the precursor. Finally, TiO_2 solution was prepared [3,22,29]. Thin film of TiO_2 was spin-coated using a standard photoresist spinner [Model: 10 MLH Plus, REMI make] at 2000 rpm for 3 minutes on the FTO glass slide which was pre-cleaned by detergent solution, water and ethanol in an ultrasonic bath. Then the glass slide was sintered at 450 ^oC for 45 min.

n-Propyl amine solution and conc. hydrochloric acid were mixed in 1:3 volume ratio. After stirring the mixture at 95 ^oC for about one hr, required amount of aqueous solution of lead acetate was added drop wise into the mixture. Calculated amount of acetic acid was added after appearance of a white precipitation. Aftermath, the solution was concentrated to saturation and cooled down to room temperature. Thus, Perovskite *n*-propyl ammonium lead chloride was prepared [3,22,29]. Finally, fabricated Perovskite material was spin coated at 2500 rpm for 30 sec on the TiO_2 layer over the FTO glass. Then again the FTO glass was heated at 90 °C for 20 min and settled to cool down gradually.

Results and discussion

Microstructure analysis

The microstructure analysis of the materials has been carried out using Scanning Electron Microscope (SEM) micrograph [Model: EVO 18 Special Edition, ZEISS make]. **Fig. 1** and **Fig. 2** display the SEM pictures of pure *n*-propyl ammonium lead chloride and *n*-propyl ammonium lead chloride deposited on TiO_2 layer respectively.

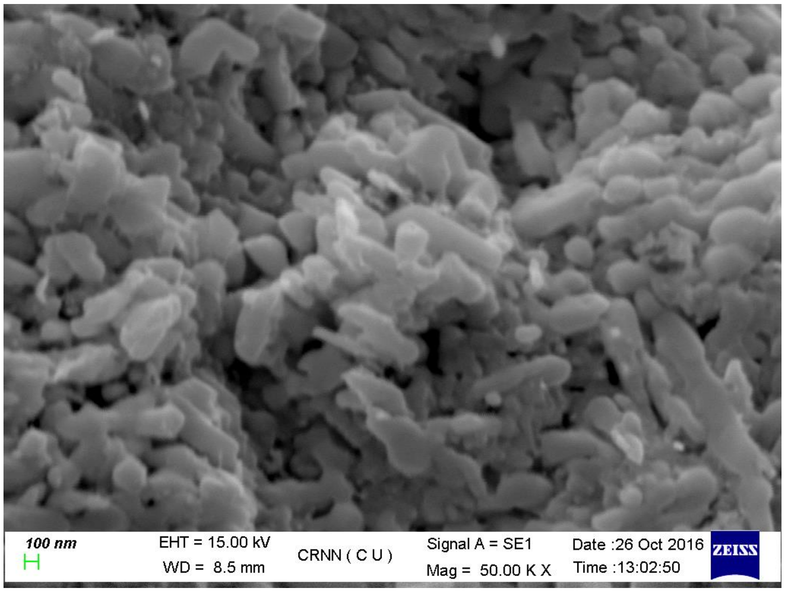

Fig. 1 SEM image of *n*-$C_3H_7NH_3PbCl_3$ without TiO_2 displays its smaller grain size

Fig. 1 represents large grain-size of *n*-propyl ammonium lead chloride. After deposition on TiO_2 layer, an appreciable morphological change of the material happened along with significant change in the grain structure of n-propyl ammonium lead chloride. The surface becomes uniform and the grain size becomes larger (around 50 nm) and more or less uniformly columnar-shaped. Perhaps, competition among the growth fronts from neighboring nucleation centers (**Fig. 2**) [18,20] results this tilted-alignment.

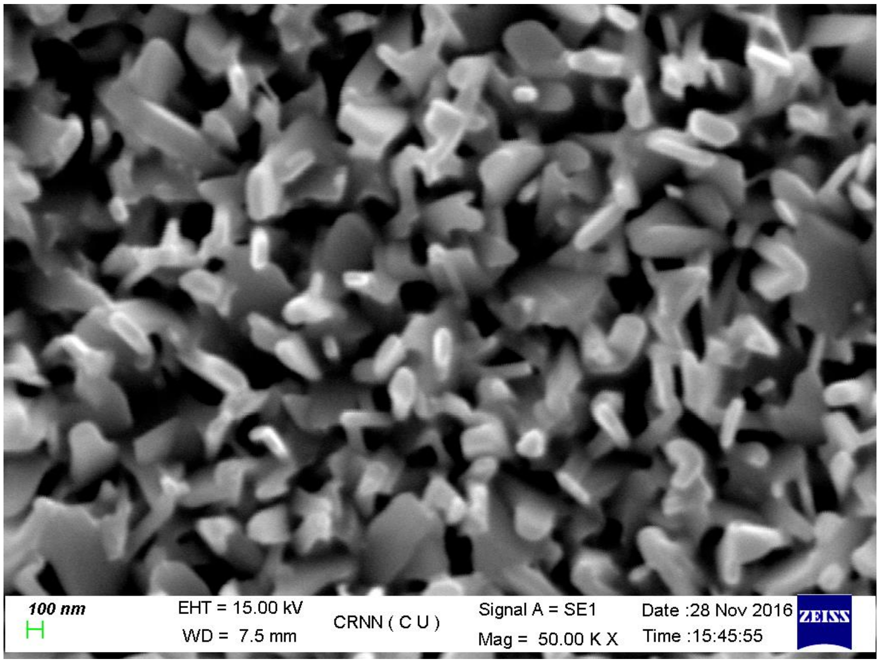

Fig. 2 SEM image of *n*-$C_3H_7NH_3PbCl_3$ with TiO_2 represents its columnar-shaped grain structure

The surface of *n*-propyl ammonium lead chloride becomes smoother and highly uniform when it is deposited on TiO_2 layer. The pores on the surface of *n*-propyl ammonium lead chloride deposited on TiO_2 layer are bit smaller. Quite large grain-size of *n*-propyl ammonium lead chloride deposited on TiO_2 layer makes this material highly polarisable and it results its higher photo-efficiency. The uniform pores help to uniform flow of electrons through the material. The *n*-propyl ammonium lead chloride deposited on TiO_2 layer is nano structured and these nano structured perovskite grains can capture sunlight in higher extent due to quite high surface to volume ratio and absorbs more photon energy [25]. The nano-material excites more and generates much excitons making the perovskite material an effective photo active matter [36,37].

XRD Analysis

The degree of crystallinity affects charge transport of a material. This parameter of the synthesized perovskite material n- propyl ammonium lead chloride was determined by using X-ray diffraction patterns on an XRD analyzer [Model: Miniflex – ZD06184, Rigaku make], equipped with a graphite mono chromator and working with CuKα (λ=1.54Å). **Fig. 3** represents the XRD pattern of the thin film, that clearly shows that the material possesses a crystalline - nature.

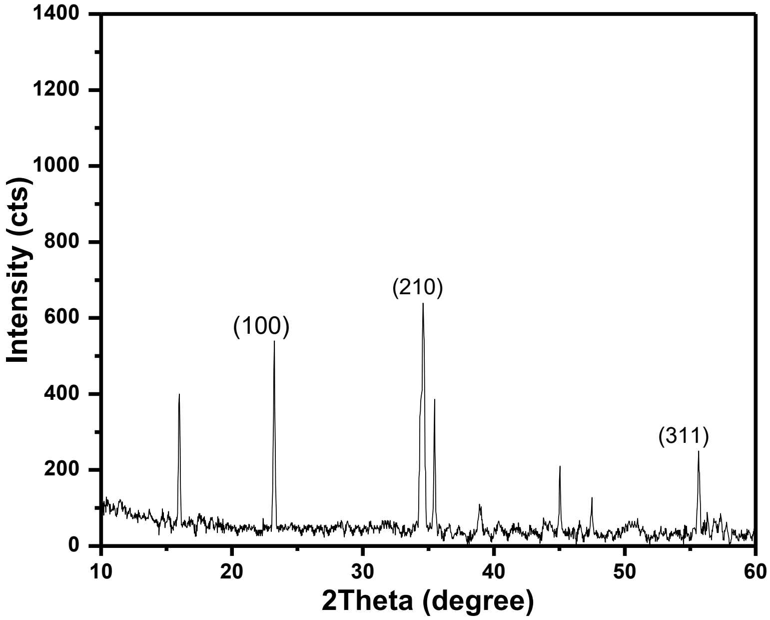

Fig. 3 XRD pattern of the perovskite material *n*-$C_3H_7NH_3PbCl_3$

The characteristic peaks at 23°, 34° and 55° corresponding to the (100), (210) and (311) planes of tetragonal perovskite ethyl ammonium lead chloride layer confirm its structure [3,22,38]. The depression of (311) plane happens perhaps due to higher extent of crystal defects present in the bulky matter.

UV-vis. spectroscopy

The study of the interaction of light with semiconducting material caters basic information regarding further photo-applicability of the material. Here, the UV–vis. spectroscopy [Model: U-4100 Spectrophotometer, Hitachi make] was performed for two materials to get an over-view about the light sensitive property of them. The UV vis. spectra (**Fig. 4**) of *n*-$C_3H_7NH_3PbCl_3$ perovskite with and without TiO_2/glass substrates show a gradual change of color.

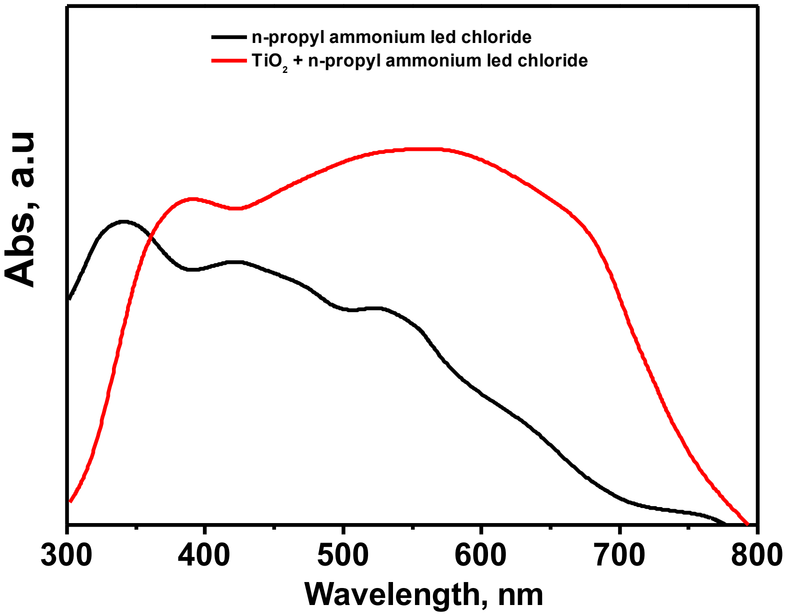

Fig. 4 UV-vis spectra of *n*-propyl ammonium lead chloride without TiO_2 and *n*-propyl ammonium lead chloride deposited on TiO_2 and band gap calculation of *n*-propyl ammonium lead chloride without TiO_2 and *n*-propyl ammonium lead chloride deposited on TiO_2.

An overall increase in intensity of the spectrum has happened when *n*-$C_3H_7NH_3PbCl_3$ coated on TiO_2 and it covers large range of spectrum (340 to 785 nm). It indicates the proper arrangement of the perovskite material n-$C_3H_7NH_3PbCl_3$ on the surface of TiO_2 and results good absorbance [25]. Moreover, mathematical calculation shows that the band gap of pure n-$C_3H_7NH_3PbCl_3$ is 1.72 eV, which is good enough to show good photo-efficiency and that of the material on TiO_2

surface is 1.50 eV. It proves that TiO_2 surface coating beneath the Perovskite material makes a change in its flat band potential and makes the material more photo-effective [3,32]. The higher crystal-defects of large propyl group and its positive inductive effect help to make the band-gap of the perovskite material on TiO_2- surface optimally low [31,39]. The working principle of the fabricated solar cell is displayed in the following schematic illustration (**Fig. 5**).

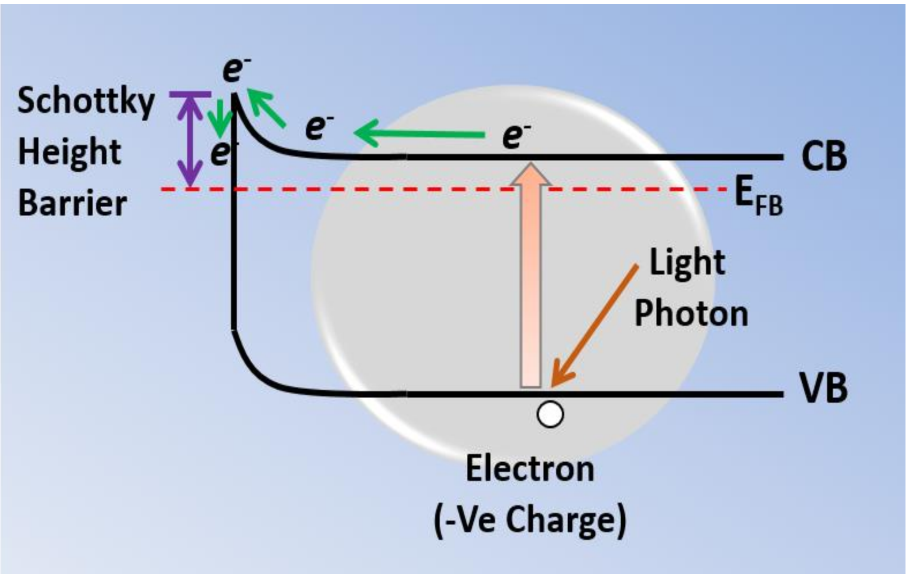

Fig. 5 The schematic representation of the working principle of the fabricated solar cell.

Photovoltaic performance

The current density-voltage ($J–V$) measurement was performed under AM1.5G standard illumination (100 $mWcm^{-2}$). The J-V parameters of the characterized photovoltaic devices are shown in **Fig. 6** and the equivalent data are presented in **Table 1**.

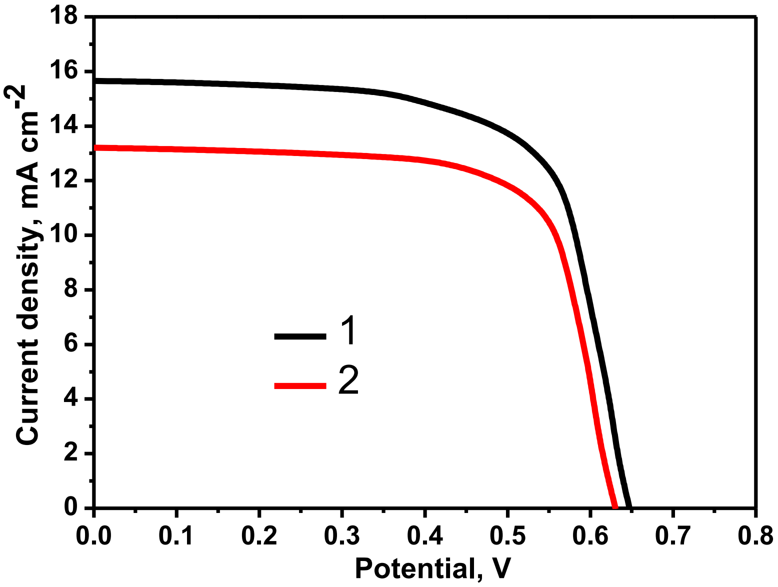

Fig. 6 The *J-V* characterization of *n*-$C_3H_7NH_3PbCl_3$ coated on TiO_2 (1) and *n*-$C_3H_7NH_3PbCl_3$ coated on TiO_2 (2) carried out under AM 1.5 G illuminations (100mW cm^{-2}).

Here, our focus was on the comparison between the newly developed *n*-propyl ammonium lead chloride deposited on TiO_2 with a reported very house-hold perovskite material which is methyl ammonium lead chloride deposited on $TiO_{2.}$ The ratio of the maximum power from the solar cell to the product of V_{oc} and I_{sc} is referred as fill factor (FF).

Table 1. Photovoltaic parameters produced from *J–V* performance of two types of photo devices under AM1.5G standard illumination (100 mWcm^{-2}). The illuminated areas of all devices were 5 cm^2.

Materials	**J_{sc} (mA cm^{-2})**	**V_{oc} (V)**	**FF (%)**	**η%**
(*n*-$C_3H_7NH_3PbCl_3$ on TiO_2)	14.2 ± (0.3)	0.617 ± (0.02)	68.2 ± (1.0)	6.01 ± (0.30)
($CH_3NH_3PbCl_3$ on TiO_2)	11.0 ± (0.3)	0.535 ± (0.05)	64.2 ± (0.9)	4.3 ± (0.40)

The "squareness" of the solar cell graphically represents the FF and it is actually the area of the largest rectangle which will fit in the IV curve. The FF of our fabricated solar cell is quite appreciable. The result presented in Table.1 confirms that the newly developed perovskite material *n*-propyl ammonium lead chloride deposited on TiO_2 surface shows higher photo conversion efficiency (η) than its previously reported methyl analogue [24,27,33] and ethyl analogue [3]. Greater extent of crystal defects present in the highly bulky *n*-propyl ammonium lead chloride is one probable factor behind its better photo-efficiency than its methyl analogue. Due to larger sized *n*-propyl group, propyl ammonium lead chloride has higher polarisibility than methyl ammonium lead chloride and ethyl ammonium lead chloride. This factor and the higher positive inductive effect of *n*-propyl group help in the better performance of the *n*-propyl ammonium lead chloride [20].

Conclusions

Through the spin coating of the solution obtained from the aqueous mixture of the reagents Lead (II) acetate, hydrochloric acid and *n*-propylamine, *n*-propyl ammonium lead chloride based thin film solar cell was fabricated successfully. The Morphological study has revealed that the thin films contain larger nano-sized particle grains (around 50 nm). XRD of the material has indicated required phase formation within it. The outcome of UV-vis. spectra showed that the synthesized material $n\text{-}C_3H_7NH_3PbCl_3$ coated on TiO_2 possessed band gap energy of around 1.50 eV. Then the photovoltaic performance of the fabricated solar cell using the synthesized material $n\text{-}C_3H_7NH_3PbCl_3$ coated on TiO_2 was tested. The value of the efficiency was around

6.01 %. This appreciable efficiency enhances the possibility to use the fabricated nano-structured substance as a very efficient solar cell material in industrial scale in the coming days.

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Conflict of interest

Author declares there is no conflict of interest regarding this publication.

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