Investigating the effects of functionalized benzylphosphonic acid SAMs on triple cation lead halide perovskite based solar cells

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Introduction

Inverted p-i-n architecture

g-ITO/NH\textsubscript{2}-BPA SAM/Perovskite/PC\textsubscript{61}BM/Au

Functionalized (R-) benzylphosphonic acid SAMs

Methodology

Nickel oxide (NiO\textsubscript{x}) nanoparticles and thin films

Ni(NO\textsubscript{3})\textsubscript{2} + NaOH
\[ \text{Ni(OH)}\textsubscript{2} + 2\text{NaNO}_3 \]

Cs\textsubscript{60}(FA\textsubscript{0.83}MA\textsubscript{0.17})\textsubscript{0.9}Pb\textsubscript{0.83}Br\textsubscript{0.17} or CsFAMA lead perovskite

FAI + MABr + PbI\textsubscript{2} + PbBr\textsubscript{2} + Csl in DMF (4) : DMSO (1)

R-BPA SAM deposition

Device fabrication

The solar cells were fabricated by spin coating NiO\textsubscript{x} nanoparticles onto the g-ITO substrates to achieve 25-30 nm thin films. The R-BPA SAMs were spin coated on the NiO\textsubscript{x} films and further rinsed using fresh acetonitrile solvent under the same spin coating conditions as for the R-BPA SAMs. The CsFAMA perovskite was spin coated on the substrates in a two-step spin coating process (10000/9000 rpm, 10/20 s) and chloroform (CB) was used as an antisolvent in the last 5 s of the spinning process followed by annealing step as expressed above. A 20 mg / mL PC\textsubscript{61}BM solution was prepared in CB for the deposition of electron transport layer. Silver was thermally deposited on top of the substrates for top electrode using a shadow mask (0.89 cm\textsuperscript{2}).

Results

Fig 1: (A) 3D-schematic for p-i-n architecture based perovskite solar cell, and chemical structures for (B) benzylphosphonic acid (BPA), (C) 4-bromobenzylphosphonic acid (Br-BPA), and (D) (4-aminobenzylphosphonic acid (NH\textsubscript{2}-BPA) molecules with dipole moments of 0.4 D, 2.3 D and ~0.9 D respectively.

Fig 2: Schematic for deposition of R-BPA SAM on g-ITO/NiO\textsubscript{x} thin films by spin coating procedure. (A) Cross sectional schematic of g-ITO/NiO\textsubscript{x} substrate before spin coating, (B) 1 spin coating of R-BPA molecules using 5 mmol / ml solution in acetonitrile followed by (B.2) rinsing of the substrate with fresh acetonitrile, and (C) cross sectional view of the final substrate with adsorbed phosphonic acid molecules. The spinning parameters for the substrates were 2000 rpm / 30 s.

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Fig 3: (A) X-ray diffraction (XRD) reflexes of prominent perovskite peaks at 14.06° (1T0) and 28.36° (220), and (B) The Ultraviolet/Visible (UV/Vis) absorbance spectra with absorbance onset at ~770 nm for CsFAMA perovskite, Br-BPA/CsFAMA, NH\textsubscript{2}-BPA/CsFAMA, and BPA/CsFAMA perovskite films on g-ITO/NiO\textsubscript{x} substrates.

Fig 4: Cross sectional (A-D) imaging for the final substrate with adsorbed phosphonic acid SAMs. The CsFAMA perovskite film and the different in crystallite sizes can be observed due to the different substrates.

Fig 5: (A) Current Density (J) - Voltage (V) curves in backward sweep direction (1.5 V to 0.1 V) for light and dark conditions, and (B) External quantum efficiency (EQE) and integrated short circuit current density (J\textsubscript{SC}) curves for reference (CsFAMA perovskite), Br-BPA, NH\textsubscript{2}-BPA, and BPA SAM modified solar cells. (C) J-V curve for reference (CsFAMA) and Br-BPA SAM modified solar cells in forward and backward sweep conditions for light and dark conditions. (D) Maximum power point (MPP) tracking data for voltage at MPP (V\textsubscript{MPP}), J at MPP (J\textsubscript{MPP}), power (P\textsubscript{MPP}), and power conversion efficiency (PCE) for the solar cells under continuous illumination for 10 min.

Fig 6: Backward scanning electron microscopy (SEM) images for CsFAMA perovskite dark and NiO\textsubscript{x} sample, a stable contact angle was observed due to Br-BPA molecules.

Table 1: Open circuit voltage (V\textsubscript{OC}), fill factor (FF), and PCE for CsFAMA perovskite and Br-BPA SAM/CsFAMA, NH\textsubscript{2}-BPA SAM/CsFAMA, and BPA SAM/CsFAMA perovskite solar cells.

Discussions

1) In Fig 3(A), the prominent perovskite XRD reflexes at 2θ = 14.06° and 28.36° confirm the presence of CsFAMA perovskite. Since the peak broadening for all CsFAMA perovskite with and without modification were within instrumental broadening, therefore, the crystallinity of the films were further investigated using SEM.

2) In Fig 3(B), absorbance onset for NiO\textsubscript{x}/CsFAMA and NiO\textsubscript{x}/R-BPA SAM/CsFAMA are at ~770 nm (~1.61 eV). No significant impact observed.

3) In Fig 4, the cross sectional (A-D) SEM images for NiO\textsubscript{x}/CsFAMA and NiO\textsubscript{x}/Br-BPA SAM/CsFAMA solar cells suggest reduced grain boundaries with in the film and the different in crystal sizes can be observed due to the different SAM molecules. The top view (A-D) SEM images for CsFAMA perovskite and Br-BPA SAM/CsFAMA, NH\textsubscript{2}-BPA SAM/CsFAMA, and BPA SAM/CsFAMA perovskite layers suggest homogeneous grain distribution across the film.

4) In Table 2, the contact angle measurements confirm the modification of the NiO\textsubscript{x} surface with different phosphonic acid molecules. The highest change in contact angle was observed due to Br-BPA molecules.

5) Inclusion of Br-BPA SAM in the solar cells improve the overall performance of the device which could be ascribed to the dipole moment of the molecules.

6) In Fig 5(B), the shape of the EQE confirms the improvement of J\textsubscript{SC} for Br-BPA SAM/CsFAMA perovskite solar cells with respect to the others.

7) In Fig 5(D), the MPP tracking data suggests that the device performance under MPP conditions for continuous illumination for 10 min is consistent and stable.

Conclusion

1) The NiO\textsubscript{x} surfaces were modified using R-BPA SAMs. The modification was confirmed using contact angle measurements and surface free energy.

2) The dipole moment of the R-BPA molecules have a significant impact on the solar cell performance.

3) The PCE of the solar cells improved with the introduction of the Br-BPA SAM in the NiO\textsubscript{x}/CsFAMA interface.

References

1. Q. Wang et al., ChemSusChem 10, 3794 (2017)

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