Exploring Methylammonium Halides as High-Efficiency Photoanodes in Solid-State Dye-Sensitized Solar Cells: A Comparative Study Using SCAPS-1D

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Abstract:

This research investigates the solar cell parameters of solid-state dye-sensitized solar cells (DSSCs) employing $MAPbCl_3$ and $MAPbBr_3$ as photoanodes. Leveraging the SCAPS-1D software, we explore the potential of methylammonium halides with elevated band gaps as viable alternatives to traditional TiO_2. Notably, $MAPbCl_3$ exhibits an efficiency of 13.78%, while $MAPbBr_3$ achieves 10.76%. The comparative study, conducted under quasi-ideal conditions, anticipates lower efficiencies in real-world experiments but remains consistent within the reliable range of DSSC solar cells.

Keywords: DSSC, perovskite, PEDOT:PSS, N719, SCAPS-1D, Solar Cell Simulation, Methylammonium Halides

Introduction:

The imperative role of energy in sustaining human life becomes increasingly apparent amid the compounding challenges of population growth and industrialization, leading to a relentless surge in energy consumption. Conventional sources such as coal, petroleum, natural gas, and hydroelectricity, once stalwarts of energy provision, now grapple with insufficiencies in meeting the burgeoning energy demands[1]. Consequently, the scientific community has fervently pursued novel and renewable energy alternatives, with solar energy emerging as a paramount and readily accessible solution. Diverse methods can harness solar energy, with solar cells standing out as a pivotal means of converting sunlight into electricity. While silicon solar cells, renowned for their efficiency, dominate the field, their prohibitive cost prompts exploration into alternatives such as Dye-Sensitized Solar Cells (DSSCs). Positioned as a cost-effective and highly efficient alternative, DSSCs have burgeoned into a new generation of photovoltaic devices. Noteworthy for their adaptability to diffused light and insensitivity to defects and recombination sites—issues plaguing other photovoltaic systems—DSSCs present a promising paradigm in the pursuit of sustainable energy solutions. [2], [3]. Their emergence underscores a transformative trajectory in the energy landscape, offering not only technical advantages but also a pathway to address the escalating energy demands of a burgeoning global population.[4], [5]

Dye-Sensitized Solar Cells (DSSCs) emulate photosynthesis, employing dye molecules in conjunction with a wide-band-gap semiconducting material as the foundational structure. The significance of the dye component lies in its role as the source of photo-excited electrons, distinguishing DSSCs from conventional cells where light absorption and charge carrier transport are separate functions. Pioneered by Michael Gratzel

and colleagues, early DSSCs utilized TiO_2 thin films and Rubipyridial complex dyes. A DSSC comprises a mesoporous semiconductor electrode with a dye adsorbed on it, a redox electrolyte, and a counter electrode [6]. The photoanode, serving as the working electrode, consists of a mesoporous layer of TiO_2 nanoparticles on a transparent substrate, typically Fluorine-doped Tin Oxide (FTO) or indium-tin-oxide (ITO). Metal-free organic dyes and metal complexes, particularly Ruthenium (II) polypyridyl complexes like N3, N719, and N749 demonstrate appreciable efficiencies. Electrolytes, crucial for regenerating dye molecules and serving as charge mediators, typically comprise organic solvents with I^-/I_3^- redox type Co (III/II) complexes or alternative options such as disulphide/thiolate (T_2/T^-) polysulfide electrolytes [7]. In solid-state DSSCs, hole transport layers like CuI, CuSCN, and PEDOT:PSS replace the traditional electrolyte. Liquid electrolytes present challenges such as evaporation, leakage, and reactions with water or oxygen, prompting the adoption of solid-state and quasi-solid-state DSSCs with high charge mobility hole transport layers like CuI, CuSCN, and PEDOT:PSS. The choice of counter electrodes, a crucial component, shifts in solid-state DSSCs, where Pt's high cost and scarcity prompt alternatives such as Ag, Au, or C [7]This strategic shift addresses issues associated with liquid electrolytes, offering a more compact and efficient solution.[8]

In conventional Dye-Sensitized Solar Cells (DSSCs), TiO_2 serves as the photoanode material due to its cost-effectiveness, abundance, non-toxicity, wide band gap, and high internal surface area for optimal dye absorption and stability. [5] However, efficiency-reducing factors, such as low electron mobility, prolonged dye adsorption time, formation of complexes with dye molecules, and high charge recombination at the photoanode-electrolyte interface, have prompted exploration into alternative materials. Perovskites, including MAPbX3 ($X=Cl^-$, I^-, Br^-) offer desirable properties as DSSC photoanodes. Represented as ABX_3, these materials exhibit characteristics such as a high absorption coefficient, low trap states, tunable optoelectronic properties, low cost, long diffusion length, high carrier mobility, and low charge recombination at interfaces. [9], [10]Compared to TiO_2, $MAPbX_3$ perovskites demonstrate higher stiffness, resulting in lower cell degradation. The direct band gap and tunability of band gap (E_g) by changing the halogen atom (X) contribute to their advantageous properties. While DSSCs can be designed and studied experimentally or computationally, simulation methods, despite their cost-effectiveness and efficiency, may yield higher values compared to real-world experiments conducted under non-ideal conditions. To mitigate discrepancies, standardizing simulation software through reproduction of similar experimental work is crucial for obtaining more reliable results. Additionally, parameters for simulation are gleaned from published experimental works and other theoretical methods, ensuring a comprehensive and accurate analysis of solar cell performance.[11]

Device simulation methodology

The Solar Cell Capacitance Simulator (SCAPS-1D), a widely utilized open-source software, represents a powerful tool for simulating various solar cell configurations. Developed by Professor M. Burgelman from the University of Gent, Belgium [12]. SCAPS-1D operates by solving five key differential equations: Poisson's equation, continuity equations for electrons and holes, and drift-diffusion equations for both electron and hole carriers. The simulation yields critical parameters such as V_{oc}, J_{sc}, FF, and PCE, accompanied by the generation of JV curves and EQE curves. This versatile software facilitates comprehensive analyses, including design, optimization, comparative studies, and performance assessments for diverse solar cell types.

In the operational mechanism of Dye-Sensitized Solar Cells (DSSCs), dye molecules absorb photons, leading to the generation of excited states (D*). Subsequent electron transfer from D* to the conduction band (CB) of the wide-band-gap photoanode initiates the photocurrent. The excited D* then transitions to a positively charged state (D^+), eventually returning to the ground state. Concurrently, in the oxidation process of the redox couple, I^- is transformed into I_3^-, releasing electrons. These electrons facilitate the regeneration of

the dye (D^+) through a series of reactions. The electrons transferred to the CB of the photoanode then move to the conducting oxide layer (TCO) and are directed towards the counter electrode through an external lead. At the counter electrode, electrons are collected by I_3^-, leading to the reduction of I_3^- and the regeneration of the electrolyte (I^-) [7]. Fig.1 shows the band diagram of the DSSC.

In solid-state DSSCs, the traditional redox couple is replaced by a hole transport layer (HTL). In this configuration, the positively charged species (D+) acquires electrons from the HTL, and the HTL is compensated by collecting electrons from the counter electrode. This innovative approach avoids the use of a redox couple, demonstrating the adaptability and versatility of solid-state DSSCs in their pursuit of enhanced performance and stability

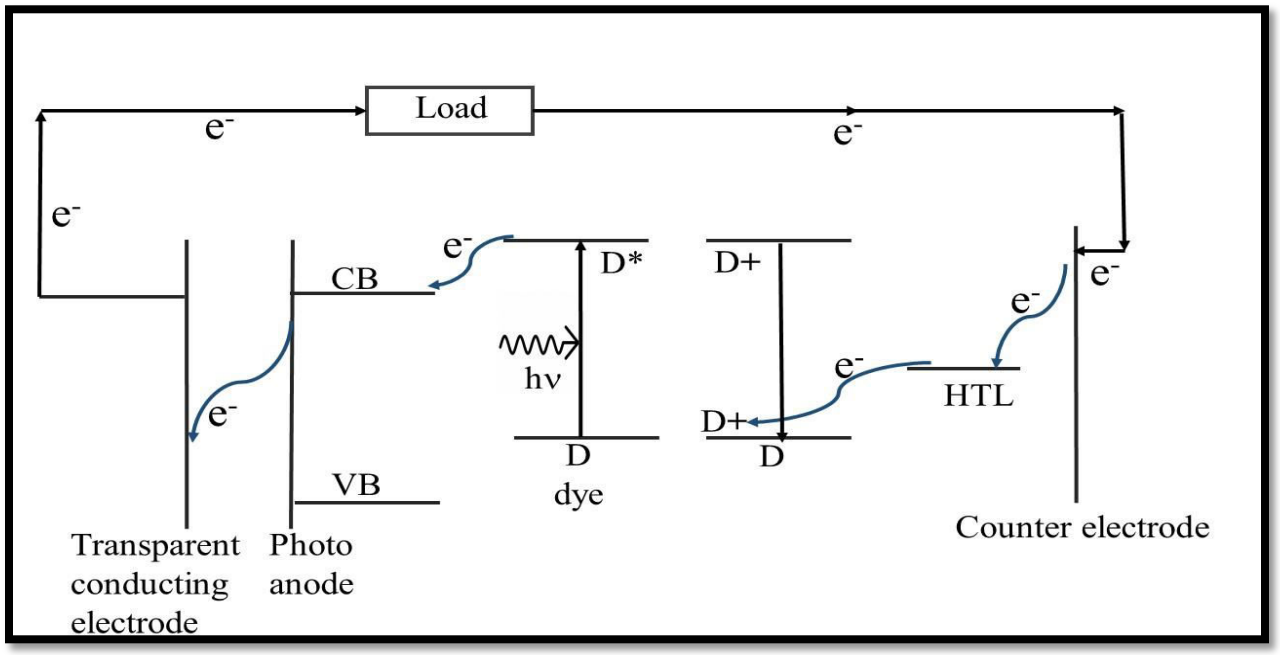

Fig.1: Band diagram of the DSSC

To yield results, the software engages in solving fundamental Poisson's and continuity equations are used as starting equations in SCAPS-1D.

$$\nabla^2\Psi = \frac{q}{\varepsilon}(n - p + N_A - N_D)$$

n=electron concentration, p=hole concentration, ε= absolute permittivity of medium, q=electron charge, ψ= electrostatic potential, N_A= acceptor concentration, N_D= donor concentration

$$\nabla \cdot \mathrm{Jn} - \mathrm{q}\frac{\partial \mathrm{n}}{\partial \mathrm{t}} = +qR$$

$$\nabla \cdot \mathrm{Jp} + \mathrm{q}\frac{\partial \mathrm{p}}{\partial \mathrm{t}} = -qR$$

R= carrier recombination rate

$\mathbf{J}_n$= electron current density

Jp= holecurrent density

$$\mathbf{J}n = qn\mu_n E + qDn\nabla n$$

$$\mathbf{J}p = qp\mu_p E - qDp\nabla p$$

E= electric field

Dn= electron diffusion coefficient

Dp= hole diffusion coefficient [13]

Results and Discussion

In this study, solid-state Dye-Sensitized Solar Cells (DSSCs) incorporating PEDOT:PSS as the Hole Transport Layer (HTL) and $MAPbCl_3$ and $MAPbBr_3$ as photoanodes were meticulously designed. The structural configurations were then subjected to simulation using the SCAPS-1D software. The validation and standardization of the software were achieved by replicating a comparable experimental setup. Two distinct cell designs, namely FTO/$MAPbBr_3$/N-719/PEDOT:PSS/Au and FTO/$MAPbCl_3$/N-719/PEDOT:PSS/Au, were specifically tailored for the investigation. Fig.2 shows the schematic arrangement of the different layers of the solar cell.

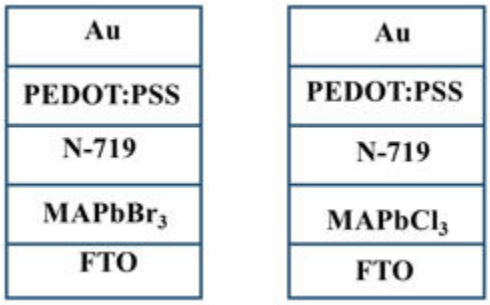

Fig.2 Schematic diagram of the different layers of the DSSC

The optoelectronic parameters utilized in this simulation were acquired from existing literature. The absorption files and fitter files were meticulously created by digitizing the relevant curves extracted from the literature. As in the Table .1.

Table 1: Different parameters used for the study

Φ Of Au=5.1eV [19]

Parameter	PEDOT:PSS	N-719	FTO	$MAPbBr_3$	$MAPbCl_3$
L	500nm	10nm	200nm	3µm	3µm
E_g(ev)	2.2	2.37	3.5	2.31	2.9[14]
χ eV)	3.6	3.9	4	3.7	3.77[15]
$\in r$	10	30	9	7.5	23[16]

Nc(cm^{-3})	10^{19}	$2.4x10^{20}$	$9.2x10^{18}$	10^{19}	10^{19}
N_V(cm^{-3})	10^{19}	$2.5x10^{20}$	$1.8x10^{19}$	10^{19}	10^{19}
Vth(e) Vth(h) cm/s	10^{7}	10^{7}	10^{7}	10^{7}	10^{7}
μ_e cm^2/vs	100	5	20	24	66[16]
μ_h cm^2/vs	0.4	5	10	24	6.6[16]
N_D(cm^{-3})	0	0	10^{19}	0	0
N_A(cm^{-3})	10^{14}	10^{17}	0	0	0
N_t(cm^{-3})	10^{16}[17]	10^{14} [17]	10^{14} [17]	10^{14}[18]	10^{14}[18]

The simulation plots are shown in Fig.2

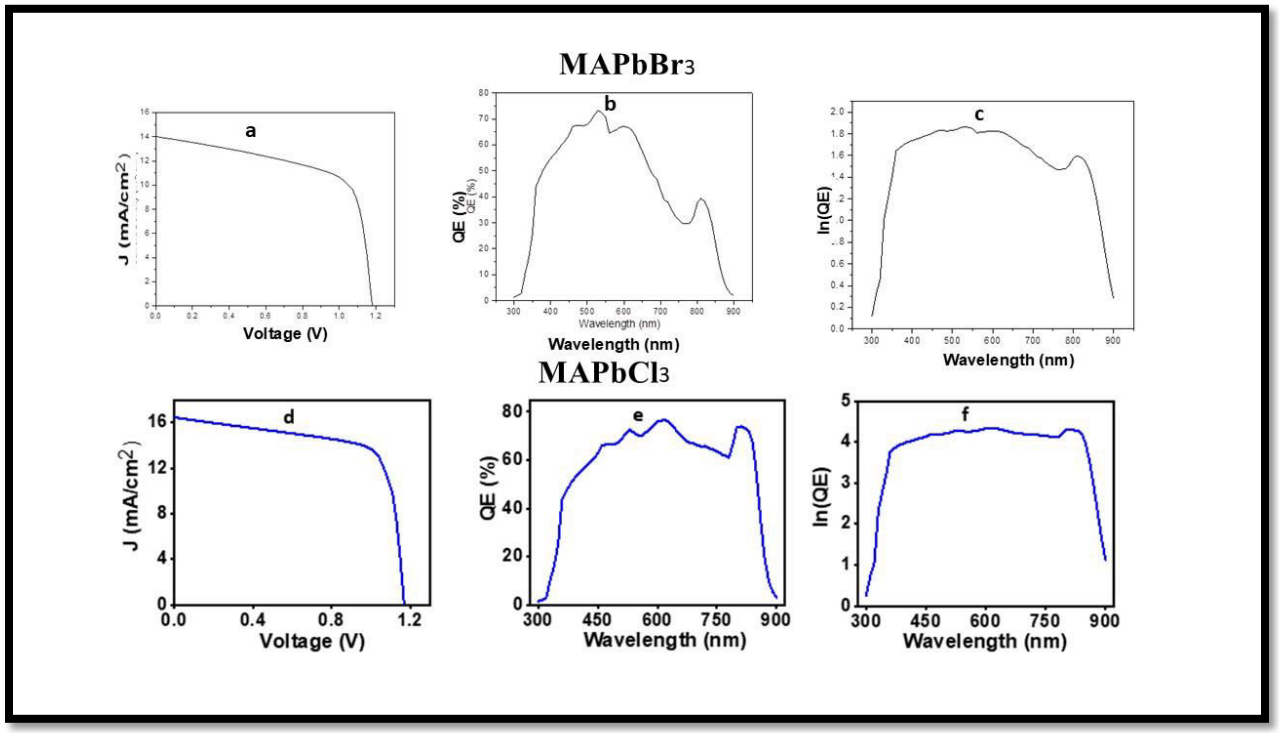

Fig.2: Simulation plots of $MAPbBr_3$ (a, b, c) and $MAPbCl_3$ (d, e, f)

Results are tabulated as given in the Table 2

Table. 2: Simulation results

Parameter	$MAPbBr_3$ Photoanode	$MAPbCl_3$ Photoanode
Voc(V)	1.18	1.17
Jsc(mA/cm^2)	14.03	16.47
FF%	64.6	71.1
PCE%	10.76	13.78

The investigation suggests that methylammonium halides with elevated bandgaps can effectively serve as Dye-Sensitized Solar Cell (DSSC) photoanodes, presenting a viable alternative to TiO_2. Specifically, $MAPbX_3$ demonstrates favorable attributes, including a high absorption coefficient, cost-effectiveness, ease of fabrication, low trap densities, tunable optoelectronic properties, and an extended carrier diffusion length. In contrast, TiO_2 exhibits drawbacks such as low electron mobility, prolonged dye absorption time, elevated carrier recombination rates, complex interactions with dye molecules, and higher costs. Notably, $MAPbI_3$, characterized by a smaller bandgap, proves impractical as a photoanode for DSSCs according to simulation results. Between $MAPbBr_3$ and $MAPbCl_3$, the DSSC featuring a $MAPbCl_3$ photoanode exhibits superior performance.

Conclusion

The investigation explores two distinct structures of solid-state Dye-Sensitized Solar Cells (DSSCs), incorporating $MAPbCl_3$ and $MAPbBr_3$ as photoanodes, revealing the potential of high-bandgap methylammonium halides as effective substitutes for TiO_2. Significantly, $MAPbCl_3$ demonstrates superior solar cell parameters compared to $MAPbBr_3$. While simulation results are conducted under ideal conditions, potentially exceeding practical values, it is anticipated that real-world applications can approach these simulated values with careful consideration of material purity and design optimization. However, the study sheds light on the impracticality of $MAPbI_3$ as a photoanode for DSSCs, owing to its smaller bandgap. Despite this setback, the research underscores the promising potential of high-bandgap methylammonium halides in enhancing the efficiency and performance of DSSCs. Looking ahead, the study propels further exploration and refinement of alternative materials, coupled with advancements in design strategies, paving the way for the development of more efficient and sustainable DSSC technologies. The findings thus open avenues for continued research and innovation in the field of photovoltaics, with the overarching goal of realizing practical applications that fully harness the potential of high-bandgap methylammonium halides in solid-state DSSCs.

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