The 28th Iranian Conference on Optics and Photonics (ICOP 2022), and the 14th Iranian Conference on Photonics Engineering and Technology (ICPET 2022).
Shahid Chamran University of Ahvaz, Khuzestan, Iran,
Feb. 1-3, 2022

لایه پروسکایت‌های دوبعدی/سه‌بعدی ترکیبی مناسب‌شده برای کاربرد سلول خورشیدی با رهیافت مهندسی افزودنی

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چکیده- در تحقیق حاضر، نمک تترابوتیل‌آمونیوم تترافلوربورات ($TBABF_4$) برای ساخت یک لایه‌ی دوبعدی/سه‌بعدی بر روی لایه‌ی پروسکایت سه‌بعدی استفاده شد. این ساختار منجر به بهبود بازده و پایداری سلول‌های خورشیدی پروسکایتی شد. برای دستیابی به بهبود بیشتر در ویژگی‌های لایه‌ی پروسکایت دوبعدی، متیل‌آمونیوم کلرید به عنوان یک افزودنی به لایه‌ی دوبعدی برپایه‌ی $TBABF_4$ اضافه گردید. رهیافت مهندسی افزودنی توانست خواص ریخت‌شناسی و نوری لایه‌ی پروسکایت دوبعدی/سه‌بعدی و همچنین خواص فوتوولتائیک سلول خورشیدی پروسکایتی دوبعدی/سه‌بعدی مرجع را افزایش دهد. بازده بیشینه ۱۸/۰۹٪ برای دستگاه‌های دوبعدی/سه‌بعدی اصلاح‌شده بدست آمد که ۱۴٪ از سلول‌های خورشیدی پایه (۱۵/۸۱٪) بیشتر است. رهیافت مهندسی افزودنی توسعه‌داده شده، بازترکیب حامل‌های بار را در لایه پروسکایت به شدت کاهش داد و فرایند انتقال حامل‌های بار در فصل مشترک لایه‌های پروسکایت و لایه انتقال‌دهنده حفره را تسهیل کرد.

کلید واژه- فوتوولتائیک، سلول‌های خورشیدی پروسکایتی، پروسکایت‌های ترکیبی، متیل‌آمونیوم کلرید

Tailored 2D/3D Hybrid Perovskite Films for Solar Cell Application with Additive Engineering Approach

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Abstract- Herein, tetrabutylammonium tetrafluoroborate ($TBABF_4$) salt was used to fabricate a 2D/3D structure over the 3D perovskite film. It raised the efficiency and stability behavior of perovskite solar cells (PSCs). To gain further enhancement in properties of the 2D/3D bi-layer, methylammonium chloride as an additive was incorporated into a 2D $TBABF_4$-based capping layer. The additive engineering approach could improve the optical and morphological properties of the 2D/3D perovskite layers and the photovoltaic performance of the reference 2D/3D PSCs. A champion power conversion efficiency (PCE) of 18.09% was obtained for the 2D/3D devices modified with the MACl additive; it was 14% higher than the fabricated reference cells (15.81%). The developed additive engineering dramatically reduced charge recombination in the perovskite film and facilitated the charge transport processes at the interface of perovskite-HTL.

Keywords: Photovoltaic, Perovskite solar cells, Hybrid perovskites, Methylammonium chloride

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1. Introduction

Up to now, perovskite solar cells' efficiency has progressively been raised to 25.5%. This ultimate achievement was reported by Min *et al.* [1] for PSCs with formamidinium lead triiodide ($FAPbI_3$) perovskite light-harvesting layer with methylenediamine dihydrochloride ($MDACl_2$) and potassium iodide (KI) additives. Different approaches have been established to obtain high-performance PSCs [2], interface engineering [3], solvent engineering [4], additive engineering [5], the improvement of the properties of electron transport layers (ETLs) and hole transport layers (HTLs) [6, 7], and the promising dimensional engineering [8].

The present study is planned for modification of 2D/3D perovskite layers by incorporating methylammonium chloride (MACl) into a 2D precursor. The proposed additive engineering approach (AEA) significantly improved the absorbance of 2D/3D perovskite layers while their band-gap energy remained constant. Besides, photovoltaic (PV) properties of the modified 2D/3D PSCs were boosted compared with the unmodified 2D/3D PSC devices.

2. Experimental

2.1. Synthesis of materials

Methylammonium halides (MACl, and MABr), formamidinium iodide (FAI), Lead iodide (PbI_2) were synthesized as our previous report [7].

2.2. Solution preparation

Cs-containing PbI_2 solution was prepared by mixing PbI_2 and $CsPbI_3$ solution, as reported in [8]. The compact TiO_2 (c-TiO_2), mesoporous TiO_2 (mp-TiO_2) were prepared as previously reported by our group [7, 8]. To improve the conductivity of the ETL, 4% (v/v) of reduced graphene oxide dispersion in dichlorobenzene (DCB, 99%, Merck) with a concentration of 1 mg/ml was poured into the diluted mp-TiO_2 precursor, followed by stirring for 60 min. The tetrabutylammonium tetrafluoroborate ($TBABF_4$, 99%, Sigma-Aldrich) precursor was prepared by dissolving 4 mg of it into 1 ml chloroform (CF, 99.8%, Merck). Besides, 4 mg of methylammonium chloride (MACl) was solved in 1 ml isopropyl alcohol (IPA, 99.8%, Merck) and added to $TBABF_4$ source as an additive at molar ratio.

2.3. Solar cells fabrication

Pre-patterned Fluorine-doped tin oxide (FTO) glasses were sequentially washed by distilled water, acetone, ethanol, and isopropanol with an ultrasonic bath. The c-TiO_2 and mp-TiO_2 layers were fabricated via spin-coating at 4000 rpm for 60 s, respectively. After each deposition step, layers were annealed at 500 ^oC for 60 min. After cooling to room temperature, perovskite layers were fabricated with a two-step method. After that, the spiro-OMeTAD solution with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.8, Sigma Aldrich) and 4-tert-Butylpyridine (TBP, 98%, Sigma Aldrich) dopants was spin-coated as hole transport layer (HTL) on top of the perovskite layers. Finally, a 100 nm gold was sputtered on the HTL as electrode layer.

3. Results and Discussions

Photoluminescence (PL), X-ray diffraction (XRD), FE-SEM, J-V techniques were employed to study the effects of the MACl additive on different aspects of 2D/3D perovskite layers. The results were consistent together, as follows.

Fig. 1a shows PL spectra of 2D/3D perovskite layers with and without MACl additive. With the incorporation of the MACl additive, a PL quenching happened, indicating facilitated charge

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Table I. Photovoltaic (PV) parameters of the pure 2D/3D perovskite solar cells (0%) and those modified with the 6% methylammonium chloride additive. To measure the average of the PV parameters, 10 devices in each group were monitored

Device		Voc[a] (V)	J_{sc}[b] (mA/cm^2)	FF[c] (%)	PCE[d] (%)
0%	Average	0.97	22.79	68.56	15.17
	Best	0.96	23.80	69.10	15.81
6%	Average	0.99	23.92	71.03	16.83
	Best	1.00	24.87	72.70	18.09

[a] Voc: open-circuit voltage; [b] Jsc: short-circuit current density; [c] FF: fill factor; [d] PCE: power conversion efficiency

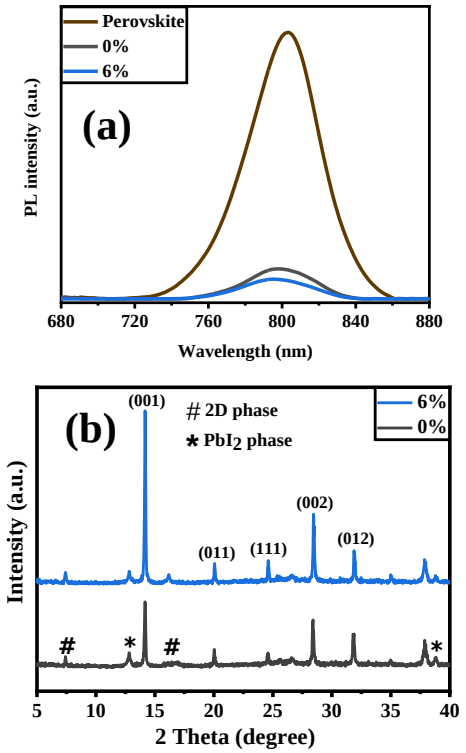


Fig 1. (a) PL spectra of different perovskite solar cells based on pure 2D/3D (0%) and modified 2D/3D perovskite layers. (b) XRD patterns of different perovskite layers coated on mesoporous TiO_2 layer

transport processes at the interface of 2D/3D perovskite and HTL layers. This suppresses charge recombination in PSCs and brings a performance improvement in PSCs (See Table I).

As can be deduced from XRD results (Fig. 1b), the MACl additive has a dual role in the mixed-dimensional 2D/3D layer formation. The suggested AEA not only boosts the orientation of the 3D perovskite film, but also increases the 2D peaks at 7.42° and 16.13°, compared with the pure 2D/3D hybrid perovskite film. This is how the additive brings about an oriented perovskite 2D/3D layer with the promising properties of both 3D and 2D perovskite layers. The results obtained from the XRD patterns are entirely consistent with the FE-SEM and PL measurements. Figs. 2a and 2b show the top-view FE-SEM images of the pure and modified 2D/3D perovskite films with the MACl additive. By employing AEA, the grain boundaries (GBs) in the 2D/3D perovskite film were passivated. It suggests that in the optimized AEA condition, an improved grain growth 2D perovskite layer is formed over the 3D perovskite layers. It is also deduced that the MACl additive creates better 2D shield layers to protect 3D perovskite layers from degradation. To check the efficacy of the AEA on the PV properties, J-V responses of different PSCs were recorded, and the corresponding PV values are listed in Table I. As shown in Fig 2c, a best-performing device with a PCE of 15.81% was recorded for the 0% 2D/3D PSCs, with the open-circuit voltage (V_{OC}) of 962 mV, the short-circuit current density (J_{SC}) of 23.80 mA/cm^2 and the fill factor (FF) of 69.1%. After the addition of 6% of the MACl to the 2D precursor, a champion PCE of 18.09% was achieved with the V_{OC}, J_{SC} and FF of 1000 mV, 24.87 mA/cm^2 and 72.7% respectively. As expected, the 2D/3D heterostructure layer improved by AEA led to higher PV performance in devices. The use of the

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MACl additive resulted in a more desirable 2D capping layer on top of the pre-formed 3D perovskite film in agreement with the XRD findings. The higher V_{OC} obtained in the modified 2D/3D PV devices was originated from the reduced trap density and suppressed charge recombination in them, which accounted for the lower PL peak in the modified 2D/3D PSCs (Fig. 1a). Besides, the improved J_{SC} and FF for the treated 2D/3D PV devices could be attributed to the suppressed hole-electron recombination, blocked direct shunting, and the improved light-harvesting ability of the 2D/3D layer. These improvements were caused by the fabrication of an oriented 2D/3D perovskite structure through the addition of the MACl dopant to the 2D precursor.

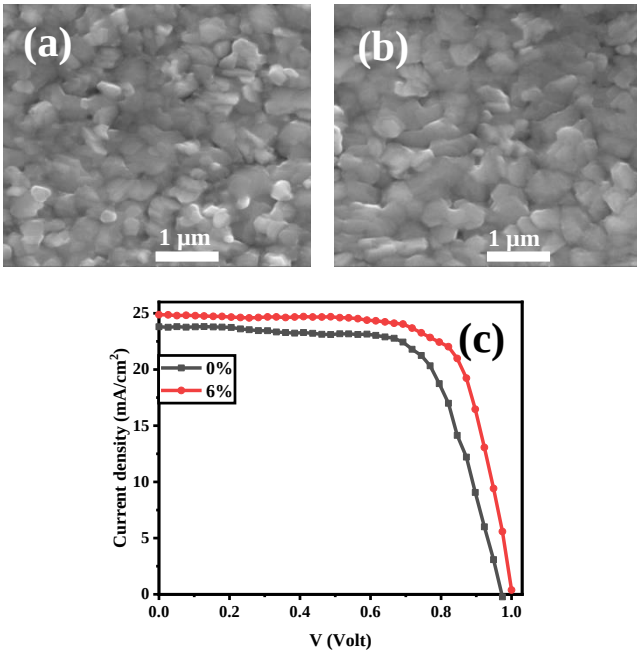


Fig 2. Top-view FE-SEM images of (a) the pure (0%) 2D/3D and (b) the 2D/3D perovskite layer modified with 6% of a methylammonium chloride solution at molar ratios. The substrate is FTO/c-TiO_2/mp-TiO_2. (c) J-V responses for the best-performing 0% and 6% 2D/3D PSCs

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