High-efficiency colorful perovskite solar cells using TiO₂ nanobowl arrays as a structured electron transport layer

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ABSTRACT The rapid development of perovskite solar cells (PSCs) has stimulated great interest in the fabrication of colorful PSCs to meet the needs of aesthetic purposes in varied applications including building integrated photovoltaics and wearable electronics. However, it remains challenging to prepare high-efficiency PSCs with attractive colors using perovskites with broad optical absorption and large absorption coefficients. Here we show that high-efficiency PSCs exhibiting distinct structural colors can be readily fabricated by employing TiO₂ nanobowl (NB) arrays as a nanostructured electron transport layer to integrate with a thin overlayer of perovskite on the NB arrays. A new crystalline precursor film based on lead acetate was prepared through a Lewis acid-base adduct approach, which allowed for the formation of a uniform overlayer of high-quality CH₃NH₃PbI₃ crystals on the inner walls of the NBs. The PSCs fabricated using the TiO₂ NB arrays showed angle-dependent vivid colors under light illumination. The resultant colorful PSCs exhibited a remarkable photovoltaic performance with a champion efficiency up to 16.94% and an average efficiency of 15.47%, which are record-breaking among the reported colorful PSCs.

Keywords: perovskite, solar cells, nanobowl arrays, structural color, nanostructures

INTRODUCTION

Organic-inorganic hybrid perovskites have aroused significant interest because of their excellent optoelectronic properties such as large absorption coefficient, long carrier diffusion length, ambipolar charge transport, and low exciton binding energy [1–3]. Impressively, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has been rapidly boosted from the initial 3.8% to 23.3% [4,5]. With the maturing of the PSC technology, it is highly desirable to develop colorful solar cells to satisfy

the requirements of aesthetic purposes in applications including building integrated photovoltaics and wearable electronics [6–9]. The broad optical absorption and the large absorption coefficient of perovskites usually lead to high-efficiency cells with dark-brown colors. Bandgap engineering has been demonstrated to be an effective approach to generate colors for PSCs [10,11]; however, it generally leads to considerably reduced PCE values (typically less than 13%) owing to diminished optical absorption associated with the enlarged bandgap [6,12].

As an alternative approach, utilization of nanostructures with engineered optical properties for color generation has attracted much more attention for fabricating colorful solar cells [13,14]. For example, colorful PSCs have been successfully fabricated using patterned perovskites films [15], such as microstructured arrays of perovskite islands [7], arrayed perovskite domains with a concentric ring photonic structure [16], and two-dimensional (2D) inverse-opal perovskite photonic films (PCE up to 12.2%) [17]. Moreover, a variety of patterned structures including dielectric mirrors [18,19], optical micro-cavities [20,21], photonic crystal (PC) scaffolds [22], plasmonic nanoresonators [23], and planar metasurfaces [24] have been employed to integrate with the photoactive perovskite layer to prepare colorful PSCs. Particularly, Park and co-workers [25] recently combined traditional optical microcavities with a dielectric functional layer, realizing 10.47%, 10.66%, and 11.18% of efficiency for red, green, and blue colored PSCs, respectively. Nevertheless, these colorful PSCs based on structural color still suffered from severe impairment of the cell performance, thus exhibiting efficiencies commonly less than 13%. It is noteworthy that Zhou *et al.* [8] realized efficient colorful PSCs by using a transparent conducting polymer as both a top electrode and a spec-

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trally selective antireflection coating. The obtained colorful PSCs displayed PEC values ranging from 12.8% to 15.1% (from red to blue) with a maximum stable PCE of 14.3% achieved for the blue colored PSC. Despite the great efforts devoted to the colorful PSCs with respectable efficiencies, it remains a challenge to realize high-efficiency, colorful PSCs through deliberate structural design.

Monolayer colloidal crystals (MCCs) or 2D colloidal assemblies have been widely employed as versatile templates for the controllable fabrication of 2D patterned micro- and nano-structures with novel optical properties such as structural color, antireflection, and multiple scattering [26–29]. It is known that both the perovskite layer [30,31] and the electron transport layer (ETL) [32,33] significantly affect the performance of the planar-heterojunction PSCs. Notably, the replication of MCCs with perovskites can lead to 2D inverse-opal perovskite photonic films or perovskite nanonets and nanobowl (NB) arrays exhibiting vivid color, which can be further used for the fabrication of high-performance photo-detectors [34] and colorful solar cells [17]. However, the reported colorful PSCs based on the deposition of perovskite NB on a planar ETL showed a limited PEC value (12.2%) [17], which could be partially related to the uneven thickness of the perovskite layer. On the other hand, the ETLs with a NB array structure have been frequently employed to fabricate efficient PSCs considering that the microstructure of the ETLs invariably affects the perovskite infiltration, light trapping and harvesting, as well as charge injection, transportation, and collection at the ETL/perovskite interfaces [35–37]. For example, Snaith *et al.* [37] pioneered in the application of NB-like ETLs by using SiO₂ honeycomb-like arrays, realizing PSCs with efficiencies up to 9.5%. Later on, Yang *et al.* [38] designed a mesoporous TiO₂ NB array with perovskite filling up the NBs to generate a flat overlayer. The resultant TiO₂ NB based devices showed a higher PCE (12.02%) compared with the planar counterpart (7.57%), mainly owing to the enhanced light absorption, improved pore-filling of high quality perovskite crystals, and increased interface contact for rapid electron extraction and fast charge transport. Recently, Song *et al.* [39] successfully realized wearable large-scale PSCs with a PCE of 12.32% *via* a MCC-templated nanocellular scaffold. The nanocellular scaffold was able to release mechanical stresses and improve the crystalline quality of the perovskite films while the nanocellular optics resonant cavity could optimize light harvesting and charge transportation. Nevertheless, all the above-mentioned PSCs with NB-like ETLs showed only dark or dark-brown colors, which could be attrib-

uted to the full coverage of the NBs by the preovskite overlayer, resulting in the disappearance of the structural color in the final cell devices. It is expected that high-performance colorful PSCs could be prepared by delicate deposition of a uniform perovskite thin layer into arrayed NBs acting as a structured ETL without jeopardizing their photonic properties.

Herein, we used TiO₂ NB arrays as a nanostructured ETL to integrate with a uniform thin overlayer of perovskite, achieving high-efficiency colorful PSCs. A new crystalline precursor film based on lead acetate was prepared through a Lewis acid-base adduct approach, which allowed for uniform deposition of the precursor thin film onto the inner walls of the TiO₂ NBs and subsequent formation of an overlayer of high-quality perovskite crystals. The PSCs based on the TiO₂ NB arrays showed vivid colors under light illumination, and the resultant colorful PSCs exhibited a remarkable photovoltaic performance with a champion efficiency up to 16.94% and an average efficiency of 15.47%, which are record-breaking among the reported colorful PSCs.

EXPERIMENTAL SECTION

Materials

Monodisperse polystyrene (PS) spheres with different diameters were purchased from Tianjin Baseline Chrom Tech Research Centre. Titanium(IV) sulfate (Ti(SO₄)₂, >96%), titanium tetrachloride (TiCl₄, >98%), and tetrabutyl titanate (TBT, >98%) were obtained from Sino-pharm Chemical Reagent Co. Hydrochloric acid (36–38 wt%) was purchased from Xilong Chemical Co. Fluoride-doped tin oxide (FTO) glass was obtained from Nippon Sheet Glass Co. Lead acetate trihydrate (Pb(OAc)₂·3H₂O, 99.99%, Aladdin), hydroiodic acid (HI, 55–58 wt% in water, contains <1.5% hypophosphorous acid as stabilizer, Aladdin), CH₃NH₂ (30–33 wt% in methanol, Aladdin), titanium diisopropoxide bis(acetylacetonate) (Ti(acac)₂OiPr₂, 75 wt% in isopropanol, Sigma Aldrich), dimethylformamide (DMF, 99.8%, J&K), dimethyl sulfoxide (DMSO, 99.8%, J&K), 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD, Advanced Election Technology Co., Ltd.), Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI, >98%, Alfa Aesar), and 4-*tert*-butyl pyridine (96 %, J&K) were used as received. All the other chemicals were of analytical grade.

CH₃NH₃I (MAI) was synthesized and purified in the lab. An aqueous HI solution (55–58 wt%) was added to a solution of methylamine in methanol (30–33 wt%) at a

desired stoichiometric ratio in a 100 mL round-bottom flask at 0°C, which was stirred for 2 h. The resultant precipitate was collected by putting the solution on a rotary evaporator and carefully removing the solvents at 50°C. Then, the raw product was redissolved in absolute ethanol and recrystallized at room temperature. The precipitate was washed with diethyl ether and dried in a vacuum oven at 50°C for 6 h.

Fabrication of PVK@TiO₂ NB arrays

FTO-coated glass substrates were first washed with detergent, rinsed with distilled water, and further cleaned with acetone and then with isopropanol. Afterwards, the substrates were dried by N₂ flow, which was followed by UV-ozone treatment for 20 min. A compact layer of TiO₂ was deposited on a cleaned substrate by spin-coating 0.15 and 0.3 mol L⁻¹ Ti(acac)₂OiPr₂ in *n*-butanol at 6000 rpm for 30 s, successively, which was then heated at 500°C for 30 min in air. The TiO₂ NB arrays were fabricated onto the FTO substrates containing the compact TiO₂ layer by interfacial lithography following the reported method [40]. The TiO₂ NB arrays on the substrates were transferred into the glove box for depositing of perovskite. The perovskite layer was deposited onto the TiO₂ NBs by spin-coating. During the spinning, a certain amount of anti-solvent chloride benzene was added onto the film, which was then annealed on a hotplate at 100°C for 1 min.

Fabrication of planar PSCs

The FTO substrates containing a compact TiO₂ layer were first fabricated as described above. The perovskite CH₃NH₃PbI₃ layer was obtained through an anti-solvent method. The precursor solution (27 wt% methylammonium lead iodide (MAPbI₃)) was prepared by dissolving Pb(OAc)₂·3H₂O and CH₃NH₃I with a molar ratio of 1:3 in a mixed solvent of DMF and DMSO with a volume ratio of 3:17. The spin-coating procedure on the FTO substrates containing a compact TiO₂ layer was performed by 6200 rpm for 40 s. After 20 s of spin-coating, 150 μL of chlorobenzene was pipetted onto the substrate. Thereafter, the substrate was put onto a hotplate for 30 min at 100°C. Subsequently, the hole-transporting material (HTM) spiro-OMeTAD was deposited on the top of perovskite by spin-coating at 4300 rpm for 30 s, giving an HTM layer (~100 nm in thickness). For the spin-coating process, the spiro-OMeTAD solution was prepared by dissolving spiro-OMeTAD in 1 mL of chlorobenzene to give a concentration of 72.3 mg mL⁻¹, which was followed by the addition of 30 μL 4-*tert*-butyl

pyridine, and 17.5 μL Li-TFSI solution in acetonitrile with a concentration of 520 mg mL⁻¹. The preparation of the compact layer was performed in ambient air and the subsequent steps were carried out in a N₂-purged glove box. At last, a gold electrode of ~70 nm in thickness was deposited on the top of the HTM layer to get the back contact through thermally evaporation under high vacuum.

Fabrication of colorful PSCs

The fabrication procedure was similar to that for the planar PSCs except using TiO₂ NB array instead of the compact TiO₂ layer as the ETL. Moreover, a thin layer of SiO₂ was deposited onto the TiO₂ NB array by a simple approach using (3-aminopropyl)trimethoxysilane (APTMS) solution following the reported method [41]. After calcination in air at 500°C for 30 min, the SiO₂-coated TiO₂ NB arrays were directly used for the deposition of the perovskite layer. It is worth mentioning that the annealing time of the preovskite precursor film was shortened to less than 1 min to avoid the perovskite decomposition. The depositions of HTM and Au electrode were the same as those for the planar PSCs, giving a spiro-OMeTAD layer of ~100 nm in thickness and a gold film of ~70 nm in thickness.

Characterization

The samples were characterized by scanning electron microscopy (SEM, Hitachi FE-S4800, 5–10 kV), transmission electron microscopy (TEM, FEI Tecnai T20, 200 kV), high resolution TEM (HRTEM, FEI Tecnai F30, 300 kV), and X-ray diffraction (XRD, Rigaku Dmax-2000, Cu Kα radiation). Reflectance spectra were recorded using an angle-resolved microspectroscopy system (ARM, ideaoptics, China) for the angle-dependent reflection and a Perkin-Elmer Lambda 950 UV/vis/NIR spectrometer for the specular reflection. Fourier transform infrared (FTIR) spectra were recorded on a Thermo NICOLET380 spectrometer. Steady state photoluminescence (PL) spectra were measured on Edinburgh Instruments (FLS 980, UK) collected at 775 nm after excitation at 470 nm. Time-resolved PL spectra were measured on Edinburgh Instruments (FLS 980, UK) with a 470 nm laser. The irradiation was generated by an Oriel solar simulator 94023A and the intensity of the irradiation was set at 100 mW cm⁻² (AM 1.5G), and the current density-voltage (*J*-*V*) characteristics were recorded on a Keithley 2400 source meter. The incident photon-to-electron conversion efficiency (IPCE) was obtained with a Crowntech IPCE testing system (Qtest station 500).

RESULTS AND DISCUSSION

Formation of PVK@TiO₂ NB arrays

Fig. 1 schematically shows the preparation process of a TiO₂ NB array covered with a perovskite thin layer (PVK@TiO₂ NB array). The TiO₂ NB arrays on a FTO glass substrate were fabricated by nanosphere lithography following the reported method [40]. Briefly, an MCC floating at the water surface was prepared by the assembly of PS spheres, which was then transferred onto the surface of a TiO₂ sol for the deposition of TiO₂ precursor, leading to the formation of an MCC@TiO₂ composite film. The MCC@TiO₂ was then transferred onto a FTO substrate and calcined at 500°C to remove the MCC template, resulting in the formation of a crystalline TiO₂ NB array. Subsequently, a perovskite precursor solution prepared by dissolving Pb(OAc)₂·3H₂O and MAI in a mixed solvent of DMF and DMSO was spin-coated onto the NB array to form a thin overlayer. After annealing at 100°C, crystallization of the precursor overlayer into the perovskite MAPbI₃ occurred, resulting in a uniform

PVK@TiO₂ NB array with periodic concavities. It may be noted that the formation of the perovskite in the presence of DMSO was *via* a Lewis acid-base approach, where polar aprotic solvents like DMSO acted as Lewis bases and formed stable adducts with the Lewis acid PbI₂ [42].

Fig. 2 shows the representative SEM images of the TiO₂ NB array and PVK@TiO₂ NB array prepared with the MCC made of 1 μm PS spheres. As shown in Fig. 2a, the TiO₂ NBs are hexagonally packed and the bottom of the NBs is very thin, showing the profile of the underlaid FTO substrate. From the tilted view in Fig. 2b, we can see holes between adjacent NBs resulting from the calcination of the PS spheres. The cross-sectional SEM image (Fig. 2c) suggests that the height of the TiO₂ NBs is about 500 nm and the thickness of the bowl wall is about 20 nm. These NBs are similar to the reported TiO₂ NB arrays prepared with 2 μm PS spheres [40]. After spin-coating and annealing of the perovskite precursor, the TiO₂ NBs were covered by a thin layer of perovskite. From the top view in Fig. 2d, we can see that the periodic NBs are retained, and the perovskite thin film is uniformly de-

Figure 1 Schematic illustration of the preparation process of PVK@TiO₂ NB array.

Figure 2 SEM images of TiO₂ NB array (a–c) and PVK@TiO₂ NB array (d–f).

posited onto the inner wall of the bowls without pin-holes. The tilted view in Fig. 2e shows obvious concave structure, which is critical to the emergence of the structural color. The cross-sectional SEM image shown in Fig. 2f suggests that the thickness of the perovskite overlayer in the bowls is about 200–250 nm.

Planar perovskite films and PSCs

It is worth noting that the composition of the perovskite precursor solution is important in controlling the crystallization processes of the perovskite, and a precursor solution with the mixed DMF/DMSO solvent is essential to the uniform deposition of a thin perovskite layer over the TiO_2 NBs. If a perovskite precursor solution made of $\text{Pb}(\text{OAc})_2$ and MAI dissolved in DMF, previously used to prepare ultra-smooth perovskite thin films and efficient planar heterojunction PSCs [43], was employed to deposit the perovskite thin films on the NBs, it was very difficult to obtain a uniform perovskite thin overlayer. Typically, some bowls were filled with the perovskite crystals while a number of bowls were still empty (Fig. S1). The uneven deposition of the perovskite thin layer on the NBs could be ascribed to the fast crystallization of perovskite compared with the relatively slow nucleation of perovskite inside the NBs. Namely, the nucleation of perovskite crystals occurred only on some bowls, which were finally filled with the grown perovskite crystals, leaving the other bowls unfilled. It was previously reported that a crystalline precursor film could be formed by using PbI_2 as the lead source and a DMF/DMSO mixture as the solvent and this Lewis acid-base approach could result in more controllable perovskite film [44,45]. In the current situation, a similar crystalline precursor film could be formed by $\text{Pb}(\text{Ac})_2$ with the mixed DMF/DMSO solvent *via* the Lewis acid-base approach, thus promoting the uniform nucleation of the crystalline precursor on all the bowls.

After annealing, the uniform crystalline precursor film would be transformed into a uniform thin perovskite layer over the inner surface of the NBs.

To investigate the role of DMSO in the crystallization processes and the characteristics of the perovskite, we fabricated perovskite thin films on planar substrates, such as FTO and bare glass, by using the precursor solutions with and without DMSO. It can be seen that the perovskite film on the FTO substrate prepared without DMSO exhibits small grains about 200 nm in size, whereas the perovskite film prepared with DMSO shows enlarged grains with sizes about 300–500 nm (Fig. S2). Notably, some bright nanoplates showing a higher contrast appeared in grain boundaries, which could be small PbI_2 crystals that are able to passivate the grain boundaries according to the previous reports [46–49].

The XRD patterns of the unannealed precursor films and the final perovskite films on the planar FTO substrate were measured to show the evolution process. As shown in Fig. 3a, the precursor film prepared without DMSO shows no diffraction peaks, indicating the formation of an amorphous film in the pure DMF solvent, which is somewhat different from the poorly crystallized precursor films obtained in DMF using PbI_2 instead of $\text{Pb}(\text{OAc})_2$ as the lead source [44,50]. When DMSO was added with a DMSO/DMF volume ratio of 3:17, which led to a DMSO/ $\text{Pb}(\text{OAc})_2$ molar ratio of 1.5:1, sharp reflections at 6.37° , 6.58° , 7.23° , 9.21° and 9.56° were observed for the precursor film, indicating the formation of a crystalline intermediate phase. This crystalline intermediate phase is reminiscent of the reported crystalline precursor crystals such as $\text{MA}_2\text{Pb}_3\text{I}_8(\text{DMSO})_2$ [44,50]. Considering that $\text{Pb}(\text{OAc})_2$ was employed instead of PbI_2 to react with MAI in the current synthesis, the current intermediate phase could adopt the formula $\text{MA}_2\text{Pb}_3\text{I}_{8-x}(\text{OAc})_x(\text{DMSO})_2$ where the I^- ions were partially substituted by

Figure 3 XRD patterns of unannealed precursor film (a) and perovskite film (b) on the FTO substrate prepared with different solvents.

the OAc^- ions. Based on the analysis using the structural analysis software Powder-X, the crystalline intermediate phase could be readily identified as a monoclinic structure with lattice parameters $a = 31.151 \text{ \AA}$, $b = 4.486 \text{ \AA}$, and $c = 27.766 \text{ \AA}$ (Table S1). After annealing at 100°C for 30 min, both precursor films turned into well-crystallized perovskite films with a tetragonal phase (Fig. 3b). For the perovskite films prepared without DMSO, a number of reflections indexed to the tetragonal MAPbI_3 crystals [51] were observed in addition to the diffraction peaks arising from the FTO substrate. In contrast, only three sharp reflections at 14.15° , 28.45° , and 43.15° were observed for the perovskite film prepared with DMSO, which corresponded to the (110), (220) and (330) planes of the tetragonal MAPbI_3 respectively. This result indicated that the perovskite film had a preferential (110) orientation with a higher crystallinity and larger grain sizes, which was consistent with the SEM result. Additionally, a very weak peak at $\sim 12.7^\circ$ corresponding to the (001) reflection of PbI_2 crystals was noticeable for the perovskite film prepared with DMSO, indicating the existence of a small amount of PbI_2 crystals in the final perovskite film, in fairly good agreement with the SEM observation. It may be noted that the small PbI_2 crystals located at the grain boundaries on the top surface are typically associated with a weak XRD reflection possibly owing to the relatively low content of PbI_2 with respect to the entire perovskite film [46–49].

A possible formation mechanism of the crystalline intermediate phase $\text{MA}_2\text{Pb}_3\text{I}_{8-x}(\text{OAc})_x(\text{DMSO})_2$ was proposed as follows. Similar to the formation of the full-coordination anion $[\text{PbI}_6]^{4-}$ [52,53], the OAc^- and I^- ions would competitively coordinate with Pb^{2+} and form a mixed full-coordination anion of $[\text{PbI}_{6-x}(\text{OAc})_x]^{4-}$. It is well known that both MAI and DMSO are Lewis bases ascribed to the presence of lone pair-electron donors (I^- for MAI and oxygen for DMSO), which tend to interact

with $[\text{PbI}_{6-x}(\text{OAc})_x]^{4-}$ to form crystalline adducts with a formula of $\text{MA}_2\text{Pb}_3\text{I}_{8-x}(\text{OAc})_x(\text{DMSO})_2$ and a defined crystal structure. The uncoordinated MAI could be stabilized by DMF. The formation of the PbI_2 crystals in the final perovskite film probably originated from the I^- deficient intermediate $[\text{PbI}_{6-x}(\text{OAc})_x]^{4-}$ that was charge-balanced by MA^+ . The presence of the Ac^- anion in the intermediate phase film was demonstrated by the FTIR spectroscopy. For the intermediate precursor film, the peak located at 1641.9 cm^{-1} could be assigned to the $\text{C}=\text{O}$ stretch in the OAc^- group, which showed obvious red shift compared with the $\text{C}=\text{O}$ stretch in $\text{Pb}(\text{OAc})_2$ probably due to the coordination effect (Fig. S3).

To gain insight into the effect of the solvents on the optoelectronic properties of the final perovskite films, UV-vis absorption, steady PL spectra, and time-resolved PL (TRPL) spectra of the planar perovskite films were measured. As shown in Fig. 4a, the perovskite film on the FTO substrate prepared with DMSO shows higher absorption below 550 nm compared with that without DMSO, which could be related to the relatively uniform and dense character of the perovskite film prepared with DMSO. For the steady and transient PL measurements, the perovskite films were directly deposited on bare glass substrates to avoid the charge injection between the perovskite film and the ETL. As shown in Fig. 4b, the PL peak is located at about 770 nm for the perovskite film prepared with DMSO, while a significant decrease in intensity and a strong red shift are observed for the perovskite film without DMSO. As documented in the literature, the decrease in the PL intensity [54] and the red shift of the PL peak [55] are mainly caused by the defects inside the perovskite crystals, indicating that the perovskite with DMSO has an improved quality. The TRPL spectra in Fig. 3c shows that the perovskite without DMSO exhibits a decay life time of 126 ns, whereas the TRPL decay rate for the perovskite film with DMSO is

Figure 4 UV-vis absorption spectra (a), steady-state PL spectra (b), and time-resolved PL spectra (c) of the planar perovskite films prepared with different solvents. Substrates: (a) FTO; (b, c) bare glass.

significantly slowed with a life time of 328 ns, indicating enlarged grain sizes and increased crystallinity originating from a crystalline precursor formed in the presence DMSO. This result suggests that the pure crystalline intermediate phase plays a key role in reducing the density of traps or defects in the final perovskite film. Moreover, the PbI_2 nanoplates at the grain boundaries could passivate the grain boundaries, thus improving the carrier lifetime.

Planar heterojunction PSCs were fabricated using the perovskite films on the FTO substrate prepared with different solvents. The cross-sectional SEM images of the planar PSCs show that there are obvious horizontal boundaries for the planar PSC prepared without DMSO whereas the perovskite crystals align well along the vertical direction and no grain boundaries exist in the vertical direction for the planar PSC prepared with DMSO (Fig. S4). The J - V curves of the planar PSCs together with a schematic of the device structure are shown in Fig. 5a. The planar PSC prepared with DMSO exhibits a PEC of 17.36%, which is much higher than 11.82% for the planar PSC prepared without DMSO. Based on the statistical results of a series of planar PSCs fabricated at each condition, an average PCE of 17.3% was achieved for the planar PSCs with DMSO, which was considerably higher than that for the PSCs prepared without DMSO (with an average PEC of 11.3%), since all the open voltage (V_{OC}), short-circuit current density (J_{SC}), and fill factor (FF) values increased noticeably with the addition of DMSO (Fig. S5). Considerable hysteresis effect was observed for these planar PSCs (Fig. S6), which probably originated from the interfacial trap states. As a result, a stabilized output efficiency of 15.8% was achieved for the PSC prepared with DMSO (Fig. 5b), and the integrated current density obtained from the IPCE measurement was somewhat lower than the J_{SC} obtained from the J - V curve (Fig. 5c). It is noteworthy that the performance of the current PSC device prepared with DMSO is higher than

all the normal planar heterojunction PSCs based on the $\text{Pb}(\text{OAc})_2$ precursor reported so far [42,52,56]. The high performance for the PSC prepared with DMSO could be attributed to the enhanced crystallinity, preferential crystal orientation, and reduced grain boundaries of the perovskite film, which could suppress the charge recombination and enhance the charge extraction at the interface. The stability of the planar PSC device prepared with DMSO was studied by storing the non-encapsulated devices at room temperature under ambient environment with relative humidity (RH) of $\sim 30\%$ – 80% for one year. The PCE dropped to $\sim 15\%$ after 14 days storage, and still retained $\sim 11\%$ after one year of storage (Fig. S7). The well aligned crystalline film and passivated grain boundaries could contribute to the enhanced stability. These results obtained from the planar perovskite films and PSCs indicate that the Lewis acid-base adduct approach based on the mixed DMF/DMSO solvent represents a promising approach for the fabrication of high-quality perovskite thin layers over TiO_2 NBs as well as high-performance planar PSCs.

Colorful PVK@ TiO_2 NB arrays and PSCs

For the investigation of the optical properties of the PVK@ TiO_2 NB array prepared using the mixed DMF/DMSO solvent, both the planar perovskite film and the PVK@ TiO_2 NB array were fabricated on a Si substrate with the mixed solvent. Under indoor illumination in ambient environment, the PVK@ TiO_2 NB array exhibited only weak and dull colors whereas the planar perovskite film looked completely dark (Fig. S8). Interestingly, upon illumination with simulated sunlight (AM 1.5G, 100 mW cm^{-2}), the PVK@ TiO_2 NB array showed vivid colors dependent on the viewing angles with respect to the direction normal to the substrate, indicating the occurrence of structural colors, whereas the planar perovskite film remained black from all viewing angles. The reflectance spectra of the PVK@ TiO_2 NB array with dif-

Figure 5 (a) J - V curves of planar PSCs prepared with different solvents. Stabilized output efficiency (b) and IPCE curve and integrated current density (c) of planar PSC prepared with DMSO.

ferent angles of emergence with respect to the direction normal to the substrate were measured under incidence of light normal to the substrate. As shown in Fig. 6a, very weak reflection peaks at around 500 nm are observed in the visible region in addition to the reflections above 700 nm, which is consistent with the naked-eye observation under indoor illumination. To further investigate the angle-dependent structural color of the PVK@TiO₂ NB array, we took photographs under perpendicular illumination of simulated sunlight (AM 1.5G, 100 mW cm⁻²) from different viewing angles, as illustrated in Fig. 6b. Actually, the PVK@TiO₂ NB array showed appealing angle-dependent vivid colors, changing from pink through green to red with increasing the viewing angle from 20° to 55° (Fig. 6c). Similar angle-dependent vivid colors were also observed for the PVK@TiO₂ NB array prepared on the FTO substrate (Fig. S9). Therefore, a wide color gamut was achieved by this novel structure of the PVK@TiO₂ NB array.

The above results suggest that an adequate intensity of an incident light is essential to obtaining obvious structural colors because the incident light is significantly absorbed by the perovskite layer and only the incident light with an adequate intensity could pass through the perovskite layer forward and backward to exhibit reflection characteristics of the periodic NB array, namely, characteristic structural colors. However, the exact origin

of the structural colors of the PVK@TiO₂ NB array remains to be elucidated because the nanostructure array is a complicated structure consisting of both the transparent TiO₂ NB array and the highly absorbing perovskite overlayer on the bowls. Our preliminary experimental results suggest that the TiO₂ NB array prepared with 1 μm PS spheres shows vivid colors even under indoor illumination and the related specular reflectance spectrum shows an obvious peak at about 472 nm (Fig. S10). Although a quantitative explanation is still lacking, the reflection spectrum and the related structural color of the TiO₂ NB array could be explained in principle by taking into consideration of the unique NB array structure using light diffraction and refraction theories [57–59]. Nevertheless, the current PVK@TiO₂ NB array is even more complicated since it combines the TiO₂ NB array and the absorbing perovskite layer. Undoubtedly, the theoretical explanation of the structural color of the unique PVK@TiO₂ NB array is worthy of further investigation.

Since the Lewis acid-base adduct approach based on the mixed DMF/DMSO solvent enabled the fabrication of high-quality PVK@TiO₂ NB array with vivid colors and the realization of high-performance planar PSCs, we attempted to prepare efficient colorful PSCs using the PVK@TiO₂ NB array prepared by this approach, where the TiO₂ NB array acted as a structured ETL. The structure of the colorful PSCs based on the PVK@TiO₂

Figure 6 (a) Reflectance spectra of PVK@TiO₂ NB array on the Si substrate with different angles of emergence. Inset shows the enlarged spectrum of the framed area. (b) Illustration of the set up for photograph collection. (c) Colorful PVK@TiO₂ NB array on the Si substrate under simulated sunlight illumination with different viewing angles. Scale bars are 0.5 cm.

NB array is schematically illustrated in Fig. 7a. Compared with the normal planar PSCs prepared with the mixed DMF/DMSO solvent, a thin SiO_2 passivation layer was deposited onto the surface of the TiO_2 NB array to passivate the perovskite/ TiO_2 interface, and the annealing time of the precursor film at 100°C was decreased from 30 min to less than 1 min to avoid decomposition of the perovskite film. It has been documented that inserting a thin isolating layer to passivate the perovskite/ TiO_2 interface can enhance the device stability [60,61]. The J - V curve of the best performing colorful PSC based on the PVK@TiO_2 NB array is given in Fig. 7b. With a J_{SC} of 22.59 mA cm^{-2} , a V_{OC} of 1.04 V, an FF of 72.0%, the PCE of the colorful PSC reaches 16.94%, which is larger than the efficiencies for all the colorful PSCs reported in the literature till now [7,8,15–25]. Specifically, the colorful PSCs with a bifunctional polymer counter electrode displayed PEC values ranging from 12.8% to 15.1% (from red to blue) [8] while most of the reported colorful PSCs exhibited PEC values less than 13%. Due to the hysteresis in the J - V measurement, the stabilized output efficiency of the solar cell was considerably lower than that of the PCE obtained from the J - V curve. After a period of light

soaking, the PCE of the colorful PSC with a SiO_2 passivation layer was stabilized to 14.1% (Fig. 7c), which was slightly lower than the maximum stable PCE of 14.3% achieved for the blue colored PSC with a polymer counter electrode [8]. It is noteworthy that compared with the colorful PSC without the SiO_2 layer, the presence of a SiO_2 passivation layer resulted in a colorful PSC showing much improved performance with significantly diminished hysteresis effect (Fig. S11). As a result, the average PCE calculated from more than ten cells was increased from 13.73% for the PSC without the SiO_2 layer to 15.47% for the PSC with the SiO_2 layer.

CONCLUSIONS

Novel PVK@TiO_2 NB arrays exhibiting vivid structural colors under light illumination were successfully fabricated by spin-coating a new crystalline precursor film onto well-defined TiO_2 NB arrays. The crystalline precursor film based on lead acetate was prepared through a Lewis acid-base adduct approach, which allowed for uniform deposition of the precursor film and subsequent formation of an overlayer of high quality perovskite crystals on the inner walls of the TiO_2 NBs. The colorful

Figure 7 (a) Schematic illustration of colorful PSC based on the PVK@TiO_2 NB array. J - V curve (b) and stabilized output efficiency (c) of colorful PSC. (d) Photographs of colorful PSC with different viewing angles. The PSC device was fabricated on $1.5 \text{ cm} \times 1.5 \text{ cm}$ FTO substrate.

PSCs based on the PVK@TiO₂ NB arrays with the TiO₂ NBs as a structural ETL exhibited a remarkable photovoltaic performance with a champion efficiency up to 16.94% and an average efficiency of 15.47%, which are higher than those for all the colorful PSCs reported so far. It is expected that the performance of the colorful PSCs based on the PVK@TiO₂ NB arrays could be further improved by delicately manipulating the patterned nanoarray structure and optimizing the deposition processes of the perovskite films. This work may open a new avenue toward high-efficiency colorful PSCs with promising applications in building integrated photovoltaics and wearable electronics.

Received 31 May 2019; accepted 3 June 2019;
published online 2 July 2019

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- Acknowledgements** This work was supported by the National Natural Science Foundation of China (21673007). The authors were grateful to Xue Zhou and Prof. Mingzhu Li for their kind help in the measurement of the reflection spectra of the perovskite@TiO₂ NB array.
- Author contributions** Qi L conceived the study. Wang W designed and performed the experiments. He Y participated in the materials preparation and data analysis. Wang W and Qi L wrote the manuscript. Qi L supervised the project. All authors contributed to the general discussion.
- Conflict of interest** The authors declare that they have no conflict of interest.
- Supplementary information** Supporting data are available in the online version of the paper.

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TiO₂纳米碗阵列作为电子传输层构筑高效率彩色钙钛矿太阳能电池

王文慧, 何雨桐, 齐利民*

摘要 钙钛矿太阳能电池的飞速发展及其在构筑一体化和可穿戴器件中的应用前景激发了人们对于彩色钙钛矿太阳能电池的浓厚兴趣, 但如何将可见光宽波段吸收且具有高吸光系数的钙钛矿材料构筑成高性能的彩色太阳能电池仍是一个挑战. 本文利用TiO₂纳米碗阵列作为结构化的电子传输层, 并在纳米碗内均匀填充一层CH₃NH₃PbI₃钙钛矿薄膜, 成功制备了具有鲜艳结构色的钙钛矿@TiO₂纳米碗阵列薄膜, 其结构色具有显著的角度依赖特征. 通过路易斯酸碱加合物法制备得到基于醋酸铅的新型晶态中间体薄膜, 使得高质量的CH₃NH₃PbI₃钙钛矿薄膜能够在纳米碗内均匀填充. 利用该钙钛矿@TiO₂纳米碗薄膜可以制备出具有鲜艳结构色的平面异质结钙钛矿太阳能电池, 其最高光电转化效率可以达到16.94%, 平均效率达到15.47%, 均高于现已报道的彩色钙钛矿太阳能电池的转化效率.