Abstract: The scaffold layer plays an important role in transporting electrons and preventing carrier recombination in mesoporous perovskite solar cells (PSCs), so the engineering of the interface between the scaffold layer and the light absorption layer has attracted widespread concern. In this work, vertically grown TiO$_2$ nanorods (NRs) as scaffold layers are fabricated and further treated with TiCl$_4$ aqueous solution. It can be found that a thin brookite TiO$_2$ nanoparticle (NP) layer is formed by the chemical bath deposition (CBD) method on the surface of every rutile NR with a low annealing temperature ($150 \, ^\circ \text{C}$), which is beneficial for the infiltration and growth of perovskite. The PSC based on the TiO$_2$ NR/brookite NP structure shows the best power conversion of 15.2%, which is 56.37% higher than that of the PSC based on bare NRs (9.72%). This complex structure presents an improved pore filling fraction and better carrier transport capability with less trap-assisted carrier recombination. In addition, low-annealing-temperature-formed brookite NPs possess a more suitable edge potential for electrons to transport from the perovskite layer to the electron collection layer when compared with high-annealing-temperature-formed anatase NPs. The brookite phase TiO$_2$ fabricated at a low temperature presents great potential for flexible PSCs.

1. Introduction

Thanks to the advantages of high absorption coefficients, broad absorption range, tunable bandgaps and long diffusion lengths, as well as the low-cost solution-processable method, the perovskite solar cell (PSC) is regarded as one of the most promising candidates for third-generation photovoltaic technologies [1–8]. After intensive efforts in interface engineering, solvent engineering, composition engineering, etc., the power conversion efficiency (PCE) of PSCs has increased from an initial 3.8% in 2009 to 25.2%, which makes it possible for PSCs to be applied in commercialization in the future [9–16]. A typical perovskite solar cell is composed of an electron transport layer (ETL), light absorption layer, hole transport layer (HTL) and counter-electrode. In addition, with the difference in the structure of the ETL, PSCs can be divided into planar and mesoporous PSCs. Compared with the planar structure, the mesoporous structure is most commonly used in PSCs owing to its slight hysteresis effect, effective carrier extraction capability as well as high stability [17–19]. A mesoporous-structure ETL contains a compact blocking layer and a scaffold layer. More importantly, the scaffold layer has been proven crucial for high-performance PSCs [20,21]. Thus, any changes or replacements in this layer will significantly affect the final performance of devices.

Inorganic metal oxides, such as aluminum oxide (Al$_2$O$_3$) [22], zinc oxide (ZnO) [23], zirconium oxide (ZrO$_2$) [24], tin oxide (SnO$_2$) [25] and titanium dioxide (TiO$_2$) [26], as the scaffold layer materials, are most commonly applied to extract photogenerated electrons from the perovskite light absorption layer to the compact layer. Among all of the materials
mentioned above, TiO$_2$, with the advantages of simple fabrication, stable crystal structure as well as high transparency, is widely employed in the state-of-the-art PSCs. Miyasaka fabricated mesoporous TiO$_2$ thin films for CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$ solar cells and obtained a PCE of 3.13% and 3.81%, respectively [10]; Park’s group achieved a PCE of 9.7% by decreasing the thickness of mesoporous TiO$_2$ and replacing the liquid electrolyte with a solid electrolyte (spiro-OMeTAD) [27]. For TiO$_2$ nanorod (NR)-based PSCs, Park investigated different lengths of rutile TiO$_2$ NRs, and an enhanced PCE from 5.9% to 9.4% was obtained [28]; Wongratanaphisan investigated the influence of the annealing temperature on the TiO$_2$ NR scaffold layer and obtained a 15.5% PCE with the TiO$_2$ NR layer treated with boiling water [29]. However, there is a non-negligible problem that PSCs based on bare NRs often suffer from internal pore filling, which will result in low light absorbance, poor interfacial transfer and unwanted carrier recombination [30,31]. To solve this problem, Haining deposited a tiny anatase TiO$_2$ nanoparticle (NP) layer to modify the surfaces of NRs by the liquid phase deposition (LPD) method and obtained a PCE of 8.61% [32]; Sawanta S prepared an ultrathin atomic layer to passivate the TiO$_2$ NRs’ surface and obtained an enhanced PCE of 13.45% [33]. Besides the methods mentioned above, TiCl$_4$ treatment is an efficient way to optimize the interface between ETL and perovskite. An nm-thick layer of TiO$_2$ NP is formed at the surface of NRs by the CBD method in a TiCl$_4$ aqueous solution, which improves the interface and creates efficient charge transfer access from the perovskite layer to ETL. However, most reports use this method with high-temperature annealing to obtain an anatase NP layer [31,34].

In this work, brookite NPs are successfully synthesized using the CBD method with a low annealing temperature on the surface of a rutile NR. Such engineering leads to a good pore filling fraction and uniform perovskite film and obtains the best PCE of 15.2%. In addition, the influence of annealing temperature on the formation of TiO$_2$ was investigated. Compared with the anatase phase formed at a high temperature, low-temperature-fabricated brookite-phase TiO$_2$ exhibits better carrier transport capability.

2. Experiment

2.1. Materials

PbI$_2$ (99.99%), CH$_3$NH$_3$I (≥99.5%), and spiro-OMeTAD (≥99.5%) were purchased from Xi’an Polymer Light Technology Corp. (Xi’an China) with no purification. TiCl$_4$ (99%), N,N-Dimethylformamide (DMF, chromatographic grade, ≥99.9%), methanol (chromatographic grade, ≥99.9%), and isopropanol (≥99.5%) were purchased from Aladdin (Shanghai, China). Hydrochloric acid (36.5–38.0 wt%) was purchased from Xilong Chemical Co. Ltd. (Guangdong, China). Tetrabutyl titanate was purchased from Tianjin Berens Biotechnology Co. Ltd. (Tianjin, China). The fluorine-doped tin oxide coated glass (FTO, 6 ohm sq$^{-1}$) was purchased from Opvtech New Energy Co., Ltd. (Yingkou, China).

2.2. Device Fabrication

The following procedures were all performed in a fume hood without any manipulation of the ambient temperature, humidity or airflow. F-doped SnO$_2$ glasses were etched with Zn powder and aqueous HCl solution, and then ultrasonically cleaned with soap, deionized water, acetone, isopropanol and ethanol in sequence, followed by a 15 min UV-O$_3$ treatment. The compact layer was fabricated through the chemical bath deposition (CBD) method in 100 mM aqueous solution of TiCl$_4$ at 70 °C for 30 min. TiO$_2$ NRs (approximately 400 nm) were grown on the as-fabricated substrates by a hydrothermal method, similar to a previous report [35]. Briefly, 30 mL distilled water was poured slowly into 30 mL hydrochloric acid (36.5–38.0 wt%) solution. Then, 1 mL tetrabutyl titanate was dropped into the mixture with constant stirring for 20 min. The mixed solution and the as-prepared TiO$_2$ layer were placed into a sealed teflon reactor (100 mL volume) for hydrothermal growth at 170 °C for 100 min. The samples were washed with deionized water and dried in the air when cooled down to room temperature. Then, samples were annealed at 450 °C for 30 min. For TiCl$_4$-treated NRs, the as-prepared samples were placed into a
0.02 M TiCl$_4$ aqueous solution at 70 °C for 30 min. Then, the samples were annealed at 150 °C, 300 °C and 450 °C for 30 min, respectively, to obtain TiO$_2$ NPs with different crystalline phases. We also treated the NRs in 0.4 M TiCl$_4$ aqueous solution at 70 °C for 60 min with 150 °C annealing to measure the phase of the NPs.

Next, 1.2 M PbI$_2$ solution (552 mg PbI$_2$ in 1 mL N,N-dimethylformamide (DMF)) was firstly dropped upon the electron transport layer (ETL) at 3000 rpm for 30 s, and then CH$_3$NH$_3$I solution (30 mg/mL in isopropanol) was spin-coated onto the PbI$_2$ layer at 5000 rpm for 30 s. The resultant perovskite film was subsequently annealed at 150 °C for 15 min. The hole-transporter layer was prepared by spin-coating spiro-OMeTAD solution at 3000 rpm for 10 s onto the perovskite layer. Finally, an 80 nm Ag layer via thermal evaporation was deposited onto the hole-transporter layer as a counter-electrode.

2.3. Characterization

The phase of synthesized samples was obtained by an X-ray diffractometer (Rigaku D/max-2500) with a 1.5418 Å Cu Kα line. The morphology and microstructure of samples were assessed by scanning electron microscopy (SEM, FEI Magellan 400). Atomic force microscopy (AFM) images were measured by an XE-7 scanning probe microscope (Park Systems, Suwon, Korea). To further demonstrate the structure of brookite nanoparticles, transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images were obtained by a JEM-2100F microscope. Ultraviolet–visible (UV–vis) absorbance spectra were measured via a spectrophotometer (UV-3150 double-beam). Steady-state photoluminescence (PL) diagrams were acquired by an HR Evolution Raman spectrometer (excitation of 473 nm at room temperature). Photocurrent density–photovoltage curves were measured by a Keithley 2400 Source Meter, and the simulated sunlight illumination (AM 1.5 G, 100 mW/cm$^2$) was provided by a 500 W xenon lamp system (CLE-S500) with a BG26M92C laser power meter to calibrate. The active area of fabricated PSCs was controlled by a mask at around 0.1 cm$^2$. Serial resistance and recombination resistance were obtained from electrochemical impedance spectroscopy (EIS) spectra using an electrochemical workstation (ZAHNER IM6, Kronach, Germany) whose frequency range was from 0.1 Hz to 100 kHz.

3. Results and Discussion

It is well known to all that some pores existing in the interior or interface between the ETL and perovskite layer could result in the poor photovoltaic performance of PSCs. Therefore, a sufficient pore filling fraction is crucial for a good PSC. Figure 1a depicts the XRD patterns of the TiO$_2$ NR/perovskite film and TiO$_2$ NR/brookite NP/perovskite film to study the effect of the brookite NPs on the crystallization of the perovskite film. Both of the samples showed three main perovskite diffraction peaks at 14.02°, 28.4° and 32.0°, which correspond to the (110), (220) and (310) crystal faces. Compared with the TiO$_2$ NRs/perovskite film, the TiO$_2$ NR/brookite NP/perovskite film presents stronger diffraction intensity, and the full width at half maximum (FWHM) diffraction peak of CH$_3$NH$_3$PbI$_3$ is smaller than that of the TiO$_2$ NR/perovskite sample, which reveals that perovskite can obtain better crystallinity after NRs are treated with TiCl$_4$. Meanwhile, an obvious diffraction peak at around 12.7°, which resulted from the residual PbI$_2$ in the perovskite film, disappeared in the TiO$_2$ NR/brookite NP/perovskite sample. This phenomenon indicates that TiCl$_4$ treatment can achieve a better reaction from PbI$_2$ and CH$_3$NH$_3$I to CH$_3$NH$_3$PbI$_3$. Moreover, to further identify the phases of the TiO$_2$ NRs and NPs, we measured the XRD patterns of bare NRs, NRs treated with 0.02 M TiCl$_4$ and NRs treated with 0.4 M TiCl$_4$, which are presented in Figure 1b. As can be seen from this figure, the rutile phase, which belongs to TiO$_2$ NRs, can be observed both in bare NRs and TiCl$_4$-treated samples at the diffraction peak at 36.08°. Expectably, there is no diffraction peak of NPs either in the bare NR sample or NRs treated with 0.02 M TiCl$_4$, which is mainly owing to the low quantity of NPs below the XRD detection limits. However, when the concentration of TiCl$_4$ is increased to 0.4 M, there are new diffraction peaks existing...
which will have a detrimental effect on the final performance of solar cells, can be observed (Figure 2e,f). The SEM images prove that the growth and formation of perovskite can be influenced by the morphology of the scaffold layer.

Figure 1. X-ray diffraction (XRD) patterns of (a) perovskite based on TiO2 NR film and TiO2 NR/brookite NP film; (b) bare NPs, NRs treated with 0.02 M TiCl4 and NRs treated with 0.4 M TiCl4.

Figure 2a,b,d,e show the cross-sectional SEM of the TiO2 NR film, TiO2 NR/perovskite film, TiO2 NR/brookite NPs film and TiO2 NR/brookite NP/perovskite film. The top-view SEM images of the TiO2 NR/perovskite film and TiO2 NR/brookite NP/perovskite film are presented in Figure 2c,f. It is obvious that TiO2 NRs grow vertically on the fluorine-doped tin oxide (FTO). After spin-coating perovskite, some pores, as carrier recombination centers, which will have a detrimental effect on the final performance of solar cells, can be observed (Figure 2b). Moreover, there are some obvious “white phase” PbI2 nanocrystals existing in the perovskite film (Figure 2c) [36,37]. As can be seen from Figure 2d, brookite NPs form a conformal layer at the surface of the NR after treatment by TiCl4. The conformal layer could form a barrier layer at the interface between perovskite and FTO to suppress charge recombination [34]. After sequential two-step spin-coating of perovskite, we notice that perovskite materials infiltrate into NRs’ interspaces, with almost no pores or PbI2 remnants (Figure 2e,f). The SEM images prove that the growth and formation of perovskite can be influenced by the morphology of the scaffold layer.

Figure 2. Cross-sectional SEM images of (a) bare TiO2 NR film; (b) bare TiO2 NR/perovskite film; (d) TiO2 NR/brookite NP film; (e) TiO2 NR/brookite NP/perovskite film; (c,f) are the top-view SEM images of bare TiO2 NR/perovskite film and TiO2 NR/brookite NP/perovskite film.

Atomic force microscopy (AFM) was used to investigate the surface roughness of the bare TiO2 NR film and TiO2 NR/brookite NP film, which are shown in Figure 3. The root-mean-square (RMS) surface roughness of the bare TiO2 NPs film is 21.2 nm, which
is smaller than that of the TiO$_2$ NR/brookite NP film (23.8 nm). The increased roughness could be attributed to the brookite NPs, which will form a rough surface for PbI$_2$ to load around the NRs and further form the perovskite layer.

**Figure 3.** Atomic force microscopy (AFM) images of (a) bare TiO$_2$ NR film; (b) TiO$_2$ NR/brookite NP film.

TEM and HRTEM were used to characterize the morphology and crystal structure of the TiO$_2$ NR and TiO$_2$ NR/brookite NPs. As shown in Figure 4a,b, the bare NR possesses a smooth surface with a length of around 400 nm. Moreover, the lattice fringes of bare NRs with an interplanar spacing $d = 0.324$ nm, which corresponds to the (110) plane of rutile TiO$_2$, can be observed in Figure 4b. This pure rutile phase indicates that the NR is a single-crystal structure with high crystallinity, which could provide direct access for photo-generated electrons to transport from the perovskite layer to the electron collecting layer. Apart from the bare rutile NR, the surface of the NR in Figure 4c is covered by NPs with a thickness of 5 nm. These NPs increase the roughness of the NR and offer a nanostructured interfacial contact between perovskite and ETL, which will promote carrier separation and transport. In addition, we notice that, besides the lattice distances of 0.324 nm, there are also existing lattice spacing values of 0.346 nm and 0.225 nm, which correspond to the (111) plane and (112) plane of brookite TiO$_2$ (JCPDS No. 29-1360) (Figure 4d). These crystalline planes and lattice spaces demonstrate that TiCl$_4$ treatment with low-temperature annealing produces a tiny uniform brookite NP layer, which covers the surface of the rutile TiO$_2$ NR.

UV–vis absorption was used to assess the absorption properties of perovskite samples with or without brookite NPs. The resulted absorption spectra (Figure 5a) reveal that both samples exhibit the same absorption onset (approximately 800 nm), yet the perovskite based on the TiO$_2$ NR/brookite NP film shows increased absorption strength, which further verifies the better growth of the perovskite film as analyzed in SEM. Moreover, the charge transport processes of the perovskite deposited on TiO$_2$ NRs and TiO$_2$ NR/brookite NP films were examined by steady-state PL spectra, as shown in Figure 5b. The FTO/TiO$_2$ NR/brookite NP/perovskite sample shows lower quenching than that of the FTO/TiO$_2$ NR/perovskite sample. This means that the TiO$_2$ NR/brookite NP structure has better capability for electron extraction and suppresses non-radiative decay [38], which is in accordance with the SEM images and photoelectric parameters. Figure 5c depicts the optimal photocurrent–voltage curves of PSCs based on TiO$_2$ NRs and TiO$_2$ NR/brookite NP ETLs under one sun AM 1.5G irradiance, and their photoelectric parameters are summarized in the figure. The power conversion efficiency (PCE) of bare NRs is 9.72%, with a short-circuit current density ($J_{sc}$) of 19.18 mA/cm$^2$, an open-circuit voltage ($V_{oc}$) of 0.962 V and a fill factor (FF) of 0.52, while the TiO$_2$ NR/brookite NP-based device shows enhanced photoelectric performance with a PCE of 15.2%, $J_{sc}$ of 21.34 mA/cm$^2$, $V_{oc}$ of 1.05 V and FF of 0.67. The enhanced $V_{oc}$ and FF could be ascribed to the less trap-assisted recombination. Meanwhile, the increased $J_{sc}$ could be attributed to the better infiltration and growth of perovskite materials. To further reveal the carrier transport as well as recombination process, EIS
measurements are carried out with a bias of 0.8 V. The Nyquist plots of two samples are shown in Figure 5d. The equivalent circuit is inserted in the figure to fit the data, where $R_s$ is the serial resistance and $R_{rec}$ is the recombination resistance of electrons in the interface between perovskite and ETL. Both $R_s$ and $R_{rec}$ can be obtained by fitting the impedance data with an equivalent circuit, and the larger semi-circle reflects higher recombination resistance and more efficient charge transport [39]. According to Figure 5d, the $R_{rec}$ of the TiO$_2$ NR/brookite NP sample (8203 $\Omega$) is larger than that of the bare TiO$_2$ NR sample (1336 $\Omega$), which indicates that brookite NPs have a positive influence on suppressing trap-assisted carrier recombination.

**Figure 4.** Transmission electron microscopy (TEM) images of (a) bare NR and (c) NR/brookite NPs; and high-resolution TEM of (b) bare NR and (d) NR/brookite NPs.

Whereas other works treated the TiO$_2$ NPs with a high annealed temperature to obtain anatase-phase NPs, we investigated the TiO$_2$ NRs with NPs annealed at different temperatures to further study the influence of temperature on NPs. Figure 6a shows the UV–vis absorption spectrum of bare TiO$_2$ NRs and TiCl$_4$-treated NRs with annealing temperatures of 150 $^\circ$C, 300 $^\circ$C and 450 $^\circ$C, respectively. The optical absorption ranges of the four samples are in the ultraviolet region. Although TiCl$_4$ treatment has little influence on the optical absorption range of the TiO$_2$, the absorption strength of TiCl$_4$-treated NRs is higher than that of bare NRs. This might be ascribed to the NPs with different annealing temperatures affecting the phase formation of TiO$_2$ and then further changing the band gap. The corresponding band gap ($E_g$) of bare rutile TiO$_2$ NRs and TiCl$_4$-treated NRs with annealing temperatures of 150 $^\circ$C, 300 $^\circ$C and 450 $^\circ$C can be calculated by the Kubelka–Munk equation [40,41], which is presented in Figure 6b. The $E_g$ of untreated TiO$_2$ NRs and TiCl$_4$-treated NRs with annealing temperatures of 150 $^\circ$C, 300 $^\circ$C and 450 $^\circ$C can be determined to be 3.22 eV, 3.17 eV, 3.20 eV and 3.19 eV. TiCl$_4$-treated NRs with an annealing temperature at 150 $^\circ$C show the narrowest energy band gap, which is similar to other reports [42].
Figure 5. (a) UV–vis absorption spectra of the TiO$_2$ NR/perovskite film and TiO$_2$ NR/brookite NP/perovskite film; (b) steady-state PL spectra of perovskite film on TiO$_2$ NRs and TiO$_2$ NR/brookite NPs, respectively; (c) J-V curves of PSCs based on TiO$_2$ NRs and TiO$_2$ NR/brookite NPs; (d) Nyquist plots of the PSCs based on TiO$_2$ NRs and TiO$_2$ NR/brookite NPs.

Figure 6. (a) UV–vis absorption spectra of TiO$_2$ NRs and TiCl$_4$-treated NRs with annealing temperature of 150 °C, 300 °C and 450 °C, respectively. (b) Corresponding band gap (E$_g$) calculated by Tauc plot.

Figure 7a–d show the statistical values for the photovoltaic parameters of 15 independent PSCs, which are based on the four different ETLs, and Table 1 provides their relevant average photovoltaic parameters. According to the outcomes, the average FF, J$_{sc}$ and V$_{oc}$ of TiCl$_4$-treated NR samples with different annealing temperatures are higher than those of bare TiO$_2$ NRs, which is mainly owing to the NRs after TiCl$_4$ treatment possessing a rough surface, which is beneficial for perovskite materials to infiltrate into the interspaces of NRs and decrease carrier recombination centers [43]. However, with the annealing temperature exceeding 150 °C, the performance of cells decreases. It might be attributed to the gradual transition of TiO$_2$ NPs from brookite to anatase, since brookite TiO$_2$ has a more suitable energy band structure than anatase, allowing for the more efficient transfer of photo-generated electrons from the perovskite layer to the rutile NRs.
Figure 6. (a) UV–vis absorption spectra of TiO$_2$ NRs and TiCl$_4$-treated NRs with annealing temperature of 150 °C, 300 °C and 450 °C, respectively; (b) corresponding band gap (E$_g$) calculated by Tauc plot.

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Figure 7. Statistical values of (a) V$_{oc}$, (b) J$_{sc}$, (c) FF and (d) PCE of PSCs based on (A) bare TiO$_2$ NR film, and TiCl$_4$-treated NR films with annealing temperature of (B) 150 °C, (C) 300 °C and (D) 450 °C, respectively.

Table 1. Average performance parameters of PSCs based on (A) bare TiO$_2$ NR film, and TiCl$_4$-treated NR films with annealing temperature of (B) 150 °C, (C) 300 °C and (D) 450 °C, respectively.

| Sample | J$_{sc}$ (mA/cm$^2$) | V$_{oc}$ (V) | FF | PCE (%) | PCE$_{best}$ (%) |
|--------|----------------------|-------------|----|---------|-----------------|
| A      | 19.16 ± 0.61         | 0.947 ± 0.029 | 0.4987 ± 0.03 | 9.09 ± 0.62 | 9.71            |
| B      | 21.57 ± 0.44         | 1.016 ± 0.054 | 0.6465 ± 0.04 | 14.16 ± 1.15 | 15.2            |
| C      | 19.99 ± 0.65         | 0.975 ± 0.018 | 0.5345 ± 0.04 | 10.42 ± 0.51 | 10.93           |
| D      | 20.49 ± 0.32         | 0.99 ± 0.019 | 0.5891 ± 0.04 | 11.98 ± 1.00 | 12.98           |

The band alignment and charge transport behavior in the TiO$_2$ NR/TiO$_2$ NP-based PSCs are illustrated in Scheme 1. As can be seen, electron–hole pairs are separated in the perovskite layer under illumination, and then electrons can transfer from the perovskite layer to the TiO$_2$ layer while holes transfer to HTL. For the poor performance of PSCs fabricated on bare NRs, the rutile-phase NRs with a single-crystal structure could provide direct accesses for photo-generated electrons to transfer. However, there are some pores that are caused by the smooth surface of the NR, existing at the interface of the perovskite layer and the NR layer. Meanwhile, photo-generated electrons are difficult to transfer to NRs due to the most negative conduction band (CB) minimum of rutile TiO$_2$ when compared to anatase and brookite [44–46]. The above reasons will finally result in poor performance. On the contrary, for PSCs fabricated on TiCl$_4$-treated NRs, the existence of NPs increases the surface coverage and thus facilitates the interfacial contact of perovskite/TiO$_2$. In the electron transfer process, rutile NR/brookite NP and rutile NR/anatase structures provide an energy level cascade, which could promote electron transfer. Since brookite NPs possess a more negative CB minimum with respect to that of anatase NPs, such an energetic structure provides better access for photo-generated electrons to transfer from perovskite to the CB of brookite NPs and then to the CB of rutile NRs. Therefore, the performance of brookite NP-based PSCs compared with anatase NP-based PSCs can be enhanced.
Scheme 1. Band alignment and charge transport behavior of PSCs based on NR and NR/NP architectures, respectively, where R, A, B and white circles indicate rutile, anatase and brookite phases of TiO$_2$ and pores, respectively.

4. Conclusions

In summary, a tiny brookite NP interfacial modification layer is successfully fabricated by the CBD method at a low annealing temperature. SEM images and PL spectra confirm that perovskite could achieve better growth and the problem of pores causing recombination is obviously improved; meanwhile, the rutile NR/brookite NP structure could form a suitable energy level cascade for electrons to transfer. PSCs based on the as-fabricated NR/brookite NP structure obtained the best PCE of 15.2% with $J_{SC} = 21.34\ mA/cm^2$, $V_{OC} = 1.05\ V$ and $FF = 0.67$, which are higher than those of bare NR-based devices. Such low-temperature-fabricated brookite nanocrystals are promising for band alignment and the cost-effective preparation of perovskite solar cells.

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