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Modification of $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ Films by $\text{NH}_2\text{-POSS}$

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Abstract: The surface composition and morphology of $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ films fabricated by the spin-coating method with different concentrations of $\text{NH}_2\text{-POSS}$ were investigated with atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), angle-resolved X-ray photoelectron spectroscopy (AR-XPS), and Fourier transform infrared spectroscopy (FTIR). It was found that the surface composition of the $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ films was changed regularly through the interaction between $\text{NH}_2\text{-POSS}$ and the perovskite film. The corresponding surface morphological changes were also observed. When the concentration of $\text{NH}_2\text{-POSS}$ exceeded 10 mg/mL, a lot of cracks on the surface of the perovskite film were observed and the surface morphology was damaged. The surface composition and its distribution can be adjusted by changing the concentration of $\text{NH}_2\text{-POSS}$ and the proper concentration of $\text{NH}_2\text{-POSS}$ can substantially improve the quality of perovskite film.

Keywords: perovskite film; $\text{NH}_2\text{-POSS}$; surface composition; morphology; photoemission spectroscopy

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1. Introduction

Hybrid organic-inorganic perovskite (HOIP) semiconductors have attracted a lot of intensive interest recently owing to their excellent advantages, such as a large absorption coefficient, long charge carrier diffusion lengths, and distinguished optoelectronic properties [1–8]. Recently, a power conversion efficiency (PCE) of 25.5% was certified by the National Renewable Energy Laboratory [9]. It is known that the stability of perovskite films is poor in wet environments, which leads to a decrease of the efficiency decrease or even failure of perovskite solar cells (PSCs). In order to obtain high-performance PSCs, a lot of studies have focused on interface engineering, such as optimizing the transmission layer material, interface control, and surface modification [10–15]. Among them, surface modification (e.g., metal ion doping and modification of common chemical additives) is one of the effective methods to improve the performance of organic-inorganic hybrid perovskite devices.

Zhou et al. explored an effective approach for simultaneous passivation of cation and anion vacancy defects in perovskite materials by adding NaF and achieved a power conversion efficiency of 21.46% [16]. Liu et al. found that a power conversion efficiency of 20.13% was realized by doping different proportions of Cs^+ in the $(\text{CH}_3\text{NH}_3)_{1-x}\text{Cs}_x\text{PbI}_3$ perovskite film [17]. Seok et al. demonstrated that the introduction of additional iodide

ions into the organic cation solution can reduce the concentration of deep defects and achieved a power conversion efficiency of 22.1% [18]. Marco et al. reported that the carrier lifetimes and open circuit voltages in hybrid perovskite solar cells can be enhanced via introducing guanidinium-based additives [19]. Snaith et al. reported that treating the crystal surfaces with the Lewis bases thiophene and pyridine can reduce nonradiative electron-hole recombination in the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite film [20]. Park et al. found that adding a tiny amount of potassium iodide to perovskite materials can greatly reduce current-voltage hysteresis and the potassium ion was best for preventing Frenkel defects as compared to other alkali metal cations [21].

Here, we introduce a new chemical additive, namely, polyhedral oligomeric silsesquioxane (POSS), which is non-toxic and tasteless, and has good biocompatibility, stability, and other characteristics. The POSS molecules have a rigid cage-like stereo structures with nanometer sizes and it can be used to prepare new organic-inorganic hybrid materials [22–25]. For example, the aminopropylsilyl POSS (NH_2 -POSS) has been used to passivate the surface of perovskite films due to its excellent chemical stability and optical properties [26]. Because the $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ polycrystalline film has obvious defects at the grain boundaries, Chen et al. reported that the NH_2 -POSS passivation at the surface and grain boundaries of perovskite film can significantly reduce the trap density and trap state energy level, which in turn enhances the PCE from 18.1% to 20.5% [27]. Some fundamental problems are still unclear, such as the change of the surface composition and the distribution of chemical components in perovskite films modified by different NH_2 -POSS concentrations.

In this study, surface modification of the $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ films was carried out by introducing the chemical additive NH_2 -POSS. X-ray, angle-resolved X-ray photoelectron spectroscopy (XPS, AR-XPS), atomic force microscopy (AFM), and Fourier transformed infrared spectroscopy (FTIR) were used to study the effects of NH_2 -POSS on the surface composition, component distribution, and surface morphology of perovskite films. It was found that NH_2 -POSS not only changes the surface composition and its distribution, but also modifies the surface morphology of the perovskite films due to the interaction between NH_2 -POSS and the perovskite. The quality of the perovskite film can be improved by using a proper concentration of NH_2 -POSS. The surface uniformity of the perovskite film is damaged when the concentration of NH_2 -POSS is above 10 mg/mL.

2. Experimental

The $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ films and NH_2 -POSS were prepared according to the reported procedure [27]. The PbI_2 solution was deposited by spin coating at 2000 rpm for 30 s and dried at 70 °C for 30 min. After the PbI_2 -coated substrate was cooled to room temperature (25 °C) in a nitrogen glovebox, a solution composed of $\text{HC}(\text{NH}_2)_2\text{I}$, $\text{CH}_3\text{NH}_3\text{I}$, $\text{CH}_3\text{NH}_3\text{Br}$, and $\text{CH}_3\text{NH}_3\text{Cl}$ was deposited by spin coating at 3000 rpm for 30 s in a nitrogen glovebox and dried at 150 °C for 15 min in air. The NH_2 -POSS solution in chlorobenzene was dropped onto the perovskite substrate, immediately followed by spin coating at 3000 rpm for 30 s, and then annealing at 100 °C for 5 min to completely remove the solvent.

The $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ films modified by different concentrations of NH_2 -POSS were sent into the characterization chamber for photoelectron spectroscopy measurements. The XPS was measured with a monochromatic Microfocus X-ray Source (Al K_{α} , $h\nu = 1486.7$ eV). For XPS, a resolution of 0.65 eV of the spectrometer was chosen with a pass energy of 40 eV. The binding energies of all XPS were calibrated and referenced to the Femi level (E_F) of the sample [28–31]. The morphology of the perovskite films was measured ex situ using an Agilent 5500AFM/SPM system. The structures of perovskites with/without NH_2 -POSS were characterized by a Fourier transform infrared spectrophotometer (Nicolet™ iS™ 50 FTIR Spectrometer; Thermo Fisher, Waltham, MA, USA) using the KBr wafer technique. All measurements were taken at room temperature.

3. Results and Discussion

The chemical structure of $\text{NH}_2\text{-POSS}$ is shown in Figure 1a, where the Si, O, H, C, and N atoms are represented by brownish-red, cyan, white, gray, and red balls, respectively. The $\text{NH}_2\text{-POSS}$ was introduced into perovskite films through a spin-coating method and the XPS full scan spectra of the perovskite films fabricated with different concentrations of $\text{NH}_2\text{-POSS}$ are shown in Figure 1b,c. The Si 2p peak appeared at about 103.81 eV when the concentration of $\text{NH}_2\text{-POSS}$ was 3 mg/mL, and the intensity of Si 2p changed consistently as the concentration of $\text{NH}_2\text{-POSS}$ was increased. In addition, the FTIR spectrum shows that the peak located at about 1103 cm^{-1} corresponds to the asymmetric stretching vibration of Si-O-Si [32] (see the Supplementary Materials Figure S1). This indicates that the $\text{NH}_2\text{-POSS}$ was successfully introduced into the surface of the perovskite films. It is also remarkable that a slight presence of the oxygen component was detected in the XPS full-scan spectra of the perovskite film without $\text{NH}_2\text{-POSS}$ modification, which can be attributed to contamination from the ex situ preparation of the sample [33].

Figure 1. (a) The chemical structure of $\text{NH}_2\text{-POSS}$. The presence of Si features is from $\text{NH}_2\text{-POSS}$. (b) The schematic scheme of the surface modification process with $\text{NH}_2\text{-POSS}$. (c) The XPS full-scan spectra of the perovskite films fabricated with different concentrations of $\text{NH}_2\text{-POSS}$.

We further analyzed the element compositions of perovskite films before and after modification by $\text{NH}_2\text{-POSS}$. In Figure 2, the I 3d_{5/2}, Pb 4f_{7/2}, and N 1s core level of the perovskite films fabricated with different concentrations of $\text{NH}_2\text{-POSS}$ are presented. For visual clarity, all the spectra were normalized to the same height. As shown in Figure 2a, the I 3d_{5/2} core level is located at about 619.55 eV (I1) for the as-grown perovskite film, corresponding to the I component in the perovskite film. After modification by $\text{NH}_2\text{-POSS}$, we observed that a new peak at about 620.74 eV (I2) appeared at the high binding energy. As the concentration of $\text{NH}_2\text{-POSS}$ increased from 3 to 20 mg/mL, the position of the I1 and I2 peak was unchanged. Similar to the I element, the Pb 4f_{7/2}-related peaks located at

about 138.78 eV (Pb1) can be attributed to the Pb component in the perovskite film, and a new peak located at about 140.23 eV (Pb2) was observed after modification by NH_2 -POSS, as shown in Figure 2b. Comparing Figure 2a with Figure 2b, it is found that the intensity of the I2 and Pb2 peaks increased with the increase of the NH_2 -POSS concentration. This indicates that NH_2 -POSS is attached to the perovskite film surface via the interaction between the amino anchoring group and the Pb-I lattice [20,34]. In Figure 2c, the N 1s core level includes more than one peak before and after modification by NH_2 -POSS for all perovskite films. For the as-grown perovskite film, the N 1s core level located at about 400.94 eV (N1) and 402.77 eV (N2) can be assigned to the N element in FA and MA, respectively. It is found that the intensity of N2 increases after modification by NH_2 -POSS, which can be attributed to the introduction of the N element in NH_2 -POSS. In addition, the full width at half maxima (FWHM) of N1 remained basically unchanged as the NH_2 -POSS concentration was increased from 0 to 20 mg/mL, while the FWHM of N2 increased from 1.14 to 2.84 eV (see the Supplementary Materials Table S1). This could be due to the interaction between NH_2 -POSS molecules and perovskite films.

Figure 2. XPS spectra of (a) I 3d_{5/2}, (b) Pb 4f_{7/2}, and (c) N 1s for perovskite films fabricated with different concentrations of NH_2 -POSS. (d) The ratio of I2/I1 and Pb2/Pb1 with different concentrations of NH_2 -POSS.

As shown in Figure 2d, the ratio of I2/I1 and Pb2/Pb1 increases as the concentration of NH_2 -POSS increased and it can be divided into two different stages. In the first stage, the ratio of I2/I1 and Pb2/Pb1 increases linearly and slowly before the concentration of NH_2 -POSS reaches 10 mg/mL. The same trend of the I2/I1 ratio and Pb2/Pb1 ratio indicated an interaction between NH_2 -POSS and perovskite film during the first stage, which agrees with previously reported results [27,34]. In the second stage, the ratio of I2/I1 and Pb2/Pb1 increases quickly with further increasing of the concentration of NH_2 -POSS, indicating that the interaction between NH_2 -POSS and perovskite film was changed. It is further proven that the compositions of the perovskite films can be affected by NH_2 -POSS.

As shown in Figure 3, the atomic concentrations of all components were plotted as a function of the concentration of NH_2 -POSS. It is observed that the atomic concentration of I1, Pb1, N1, and C3 decreases as the concentration of NH_2 -POSS increases, which can be attributed to the surface modification with NH_2 -POSS. As shown in Figure 3a,b, the atomic concentration of I1 is about 12% and 6% at 0° and 60° (take-off angle), respectively, when the concentration of NH_2 -POSS is 3 mg/mL. It is the same for the components Pb1, N1, and C3, which come from the perovskite film. In Figure 3b, the atomic concentration of Si is about 23% at 3 mg/mL NH_2 -POSS. It increases to about 25% at 5 mg/mL and then slightly increases as the concentration of NH_2 -POSS increases, which is the same for C1, Si, and O from NH_2 -POSS. Otherwise, the content of I2 and Pb2 increases slowly as the concentration of NH_2 -POSS increases, as shown in Figure 3a,b. It indicates that there

is interaction between $\text{NH}_2\text{-POSS}$ and the perovskite film, mostly on the surface of the perovskite film.

Figure 3. Atomic concentration of all components in the perovskite films as a function of the concentration of $\text{NH}_2\text{-POSS}$. (a) The take-off angle is 0° ; (b) the take-off angle is 60° .

The relative depth plot of the chemical components of perovskite films fabricated with different concentrations of $\text{NH}_2\text{-POSS}$ is shown in Figure 4. For the as-grown perovskite film, it is observed that the C3 component has a smaller relative depth, the I1 component has a greater relative depth, and the N1 and Pb1 components have a moderate relative depth, as shown in Figure 4a. After modification by $\text{NH}_2\text{-POSS}$, the Si, O, and C1 components have a smaller relative depth; and the Pb2 component has a greater relative depth when the concentration of $\text{NH}_2\text{-POSS}$ is 3 or 5 mg/mL, as shown in Figure 4b,c. With a further increase of the concentration of $\text{NH}_2\text{-POSS}$, the Pb2, Si, C1, and O components have a smaller relative depth. When the concentration of $\text{NH}_2\text{-POSS}$ reaches 10 mg/mL, the relative depth of Pb2 changes significantly, as shown in Figure 4d. This indicates that the interfacial reaction between $\text{NH}_2\text{-POSS}$ and superficial perovskite is complete and the Pb2 is mostly on the surface. As the take-off angle reaches 60° , the content of Pb2 remains basically unchanged and that of Pb1 decreases, so Pb2 has a smaller relative depth. The relative depth of Pb1, I2, N1, and I1 remains almost unchanged at the concentration of 10 mg/mL. This can be attributed to the interaction between the perovskite film and $\text{NH}_2\text{-POSS}$, which has an influence on the surface composition and its structure.

Figure 5 shows the surface morphologies of the perovskite films fabricated with different concentrations of $\text{NH}_2\text{-POSS}$ investigated using AFM. The height profiles correspond to the height variation of the blue line in the AFM images. It can be clearly observed that the surface morphologies of the perovskite films are changed by $\text{NH}_2\text{-POSS}$. The morphology of the as-grown perovskite film is shown in Figure 5a. Crystalline particles are found on the surface, and the corresponding root mean square (RMS) is 24.87 nm. After the modification by $\text{NH}_2\text{-POSS}$, the surface morphologies of the perovskite films were changed significantly and no crystalline particle was observed on the surface, as shown in Figure 5b–f. When the concentration of $\text{NH}_2\text{-POSS}$ is 10 mg/mL, the RMS is about 12.43 nm, which is the lowest value of all modified perovskite films. It is noticeable that there are a lot of cracks on the surface of the perovskite films, and the height profile is obviously concave downward when the concentration of $\text{NH}_2\text{-POSS}$ exceeds 10 mg/mL, as

shown in Figure 5e,f. It suggests that the NH_2 -POSS can damage the surface morphology when the concentration of NH_2 -POSS is 15 and 20 mg/mL, which will lead to a decrease of the device's performance. As a matter of fact, the best device performance was obtained after modification with 10 mg/mL NH_2 -POSS in a previous study [27].

Figure 4. Relative depth plot of the chemical components of perovskite films fabricated with different concentrations of NH_2 -POSS.

Figure 5. AFM images of perovskite films fabricated with different concentrations of NH_2 -POSS. The height profiles correspond to the height variation of the blue line in the AFM images.

Figure 6 shows the device performances of perovskite films modified with a NH_2 -POSS concentration of 0, 3, 5, 10, 15, and 20 mg/mL. It is well known that the most important parameters for the PSCs are open-circuit (V_{oc}), short-circuit (J_{sc}), fill factor (FF), and power conversion efficiency (PCE). As shown in Figure 6d, we found that the best PCE of the perovskite solar cells is about 17.40% when the NH_2 -POSS concentration is 10 mg/mL. According to the box distribution of these parameters, we found that V_{oc} increases as the concentration of NH_2 -POSS increases from 0 to 10 mg/mL, which reduces the recombination of the carrier at the interface and improves the corresponding J_{sc} . Thus, the perovskite film modified with 10 mg/mL NH_2 -POSS shows the best device performance. This indicates that the changes of the surface morphology and composition of the perovskite films are closely related to the device's performance. Similarly, the PCE of the perovskite solar cell increases to 15.6% from 13.3% by introducing an appropriate POSS passivation layer between the perovskite and hole transporting layers, which is useful to significantly increase the grain size of the perovskite film and also increase the short-circuit current and open-circuit voltage [35]. Otherwise, the electronic structure and surface composition of perovskite films can be adjusted by the incorporation of CsPbBr_3 nanocrystals, and the photovoltaic performance of the perovskite solar cell is enhanced [36]. Thus, a good way to improve the device performance is by adjusting the surface properties of the perovskite film.

Figure 6. Photovoltaic metric for perovskite solar cells fabricated with different concentrations of NH_2 -POSS. (a) open-circuit (V_{oc}), (b) short-circuit (J_{sc}), (c) fill factor (FF), and (d) power conversion efficiency (PCE).

4. Conclusions

In summary, we investigated the surface morphology, surface composition, and distribution of $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ films after modification by different concentrations of NH_2 -POSS using AFM, XPS, AR-XPS, and FTIR. It was found that the surface composition and morphology of perovskite films can be influenced by NH_2 -POSS. The surface composition and its distribution can be adjusted by changing the concentration of NH_2 -POSS. The surface morphology of the perovskite film was damaged when the concentration of NH_2 -POSS exceeded 10 mg/mL. Thus, the proper concentration of NH_2 -POSS would improve the quality of perovskite film. Our analysis provides insight for the underlining mechanisms of controlling the properties of perovskite films by adjusting the concentrations of the modified materials, which will be useful for improving the performances of perovskite solar cells.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/cryst11121544/s1>, Figure S1: FTIR spectrum of perovskite with/without NH₂-POSS; Table S1: XPS fitting data for perovskite films fabricated with different concentration of NH₂-POSS.

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