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Rigid amino acid as linker to enhance the crystallinity of CH₃NH₃PbI₃ particles

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Organic-inorganic hybrid perovskites have attracted extensive interest in recent years due to their remarkable properties in highly efficient solar cells. The quality of the perovskite thin films has been identified as a critical factor to affect the performances of the solar cells. To achieve uniform and dense perovskite films, many efforts have been attempted on controlling the crystallinity of the particles, grain size, as well as surface coverage. Using organic coupling agents to connect the mesoporous TiO₂ with the perovskite film was an effective way to guide the growth of perovskite film. However, the influences of organic molecular configurations on the perovskite crystallization are still not being well studied. In this article, we employ two amino acids, 4-aminobenzoic acid and 4-aminobutyric acid, with similar molecular size and closed chain length to study the molecular rigidity of the organic coupling agents affecting the quality of perovskite films. Greatly improved perovskite film has been obtained with the template effect of rigid 4-aminobenzoic acid and thus the cell performance has been significantly increased.

Keywords: (organic-inorganic hybrid perovskites, solar cells, rigid molecule, amino acids)

1.

Introduction

Hybrid organometal trihalide perovskites ($\text{CH}_3\text{NH}_3\text{PbX}_3$, $\text{X} = \text{Cl}^-$, Br^- , and I^-) have attracted extensive interest in recent years due to their excellent optoelectronic properties, such as intense light absorption, long charge carriers life time and diffusion length, and small exciton binding energies.^[1-9] Particularly, solar cells based on this kind of perovskites as light harvesters have developed rapidly. So far, the power conversion efficiency has certified to be as high as 22.1% within merely few years.^[10] Typically, a regular architected perovskite solar cell (PSC) contains a compact TiO_2 thin layer, a mesoporous TiO_2 film, a perovskite layer, and a hole transporting material layer.^[11-14] As the heart of the PSC, the quality of the perovskite film plays a critical role on determining the cell performance. Incomplete surface coverage of perovskite film on the TiO_2 layer and plenty defect-assisted traps in the perovskite film can greatly reduce the performance of devices.^[15] Therefore, many efforts have been attempted to produce uniform perovskite thin films with big grain size and high crystallinity.

To achieve better control over the morphology of perovskite films, a few of amphiphilic organic coupling agents have been separately employed to guide the formation of perovskite film. For example, Ogomi and co-workers used $\text{HOCO-R-NH}_3^+\text{T}^-$ ($\text{R}=1, 2, 3$) as an anchor to link the mesoporous- TiO_2 film and the perovskite layer and an increase of the power conversion efficiency (PCE) from 8% to 10% was achieved for the solar cell.^[16] Shih *et. al.* applied glycine as a coupling agent to modify the $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ interface and a significant improvement of PCE for the solar cells from 8.35% to 12.02% was obtained.^[17] Other parallel studies using either 3-aminopropanoic acid or 4-aminobenzoic acid (PABA), which have been conducted by Chen *et. al.* and Huang *et. al.*, separately demonstrate that such organic linkers can greatly enhance the crystalline of perovskite particles and improved the

quality of the film, and thus improved the performance of perovskite solar cells.^[18,19]

However, the effects of molecular configurations of the organic coupling agents on the forming of the perovskite have seldom been studied.

Herein, we used two amino acids, rigid 4-aminobenzoic acid (**Figure 1**) and flexible 4-aminobutyric acid (GABA, **Figure 1**), with similar molecular size and closed chain length as coupling agents and studied the influence of molecular rigidity on both crystallization of the perovskite particles and quality of perovskite films. Perovskite films prepared using PABA as the coupling agent showed better crystallinity and improved film flatness compared with those treated by GABA. The PCE of PABA treated cell was increased from 13.6% up to 16.8% comparing to the untreated cell, mainly due to the enhancement of the short-circuit current density (J_{sc}) from 19.12 to 22.00 mA cm⁻². Meantime, the efficiency and J_{sc} are respectively 6% and 3% higher than those of the GABA treated solar cell.

2. Results and Discussion

In order to introduce the coupling agents on the mesoporous TiO₂ films, the porous substrates were dipped respectively in a solution with 5 mM GABA or PABA in ethanol for 2 h. Then, the samples were washed with ethanol to remove the unchelated residuals and dried under vacuum. The infrared (IR) spectra were measured to determine whether the coupling agents anchored onto the mesoporous TiO₂ films. For the case of PABA coated films, strong peaks observed at 1177 cm⁻¹, 1395 cm⁻¹ and 1620 cm⁻¹ can be ascribed to the C–O stretching and C=O stretching, corresponding to the COO- group of the molecules; and the peaks appeared at 1284 cm⁻¹ and 3342 cm⁻¹ can be ascribed to -NH₂ group. This confirmed that the PABA molecules were anchoring on the mesoporous TiO₂ films by COO- group. The IR spectrum of GABA coated sample showed peaks at 1400 cm⁻¹ and 1300 cm⁻¹ which are ascribed respectively to the ester group and the amine group, indicating the GABA molecules were

also linking to the mesoporous TiO₂ films. The much stronger peaks observed in PABA treated sample may be attributed to the larger amount of PABA molecules adsorbing on the TiO₂ film than the GABA molecules since the PABA molecules are more rigid compared with GABA molecules and therefore can array on the mesoporous TiO₂ film more densely. Subsequently, the CH₃NH₃PbI₃ (MAPbI₃) films were spin-coated on the coupling agents coated substrates. The IR spectra of the TiO₂/MAPbI₃ films were measured again to determine whether the coated coupling agents were washed away by the perovskite precursor solution. The presence of vibrational peaks at 1180 cm⁻¹, 1395 cm⁻¹ and 1620 cm⁻¹ of the IR spectrum of TiO₂/PABA/MAPbI₃ film (**Figure 2a**) shows clearly that the plenty of PABA molecules were still anchoring on the TiO₂ film even after deposition of the MAPbI₃ film. However, for the case of TiO₂/GABA/MAPbI₃ film, the characteristic peaks of GABA at around 1309 cm⁻¹ and 1405 cm⁻¹ cannot be easily observed (**Figure 2b**), indicating very few GABA molecules were on the TiO₂ film after the spin-coating of the MAPbI₃ film. The vast differences in IR spectroscopies of TiO₂/PABA/MAPbI₃ and TiO₂/GABA/MAPbI₃ films suggested that the PABA molecules linked to the mesoporous TiO₂ film stronger than the GABA molecules.

In **Figure 3**, we compare the X-ray diffraction (XRD) patterns of the MAPbI₃ films on TiO₂ without and with PABA and GABA as coupling agents. The main diffraction peaks at 2θ of 14.44° and 29.12° assigned to the (110) and (220) lattice planes were observed in identical positions for the MAPbI₃ films formed at the three different conditions, indicating that the coupling agents at the TiO₂/MAPbI₃ interface didn't change the orthorhombic crystal structure of the perovskite.^[14] In the meanwhile, a close inspection on the XRD patterns shows that stronger diffractions at (110) and (220) lattice planes for the MAPbI₃ films with coupling agents comparing to the film directly deposited on TiO₂ film. The strong peaks of

(110) and (220) lattice planes generally suggest good crystallinity of the MAPbI₃ films.^[14]

Hence, the use of PABA and GABA as coupling agents on the TiO₂ surface can improve the crystallization of the perovskite. Further comparison of the XRD patterns of perovskite films treated with two coupling agents show that the diffraction peaks of MAPbI₃ film with PABA as coupling agent were slightly stronger than those of the film templated by GABA. This confirmed that from the viewpoint of enhancing the MAPbI₃ crystallization, the rigid PABA might be more efficient than the flexible GABA. These results were further confirmed by the micrographs of the MAPbI₃ films. The top-view scanning electron microscopy (SEM) images of the MAPbI₃ films grown on bare-TiO₂ film and with the amino acids as coupling agents are shown in **Figure 4**. Without coupling agent treatment, the MAPbI₃ film consisted of nanoparticles with grain sizes varied in a broad range of 100–800 nm in relatively poor crystallinity. Therefore, the surface of the film was not dense and contained many voids. In contrast, with the coupling agents treating the TiO₂ films substrate, the MAPbI₃ films displayed more uniform and dense morphologies with less voids. The distribution of particle sizes was narrowed to 200–500 nm. It was reasonable to deduce that the coupling agents induced the perovskite particles grow more uniformly. Specifically, PABA treated MAPbI₃ film showed more uniform and compact morphology, possibly owing to the more regular array of rigid PABA molecules on the TiO₂ surface that leads to the perovskite particles grow more densely.

The effect of the coupling agents on the solar cell photovoltaic performance was investigated by comparing solar cells without and with the coupling agent treatment. For each condition, 20 cells were prepared for measuring the current density–voltage ($J-V$) characteristic curves. The $J-V$ characteristic curves were performed under standard AM 1.5 simulated solar irradiation and the work area of the solar cells was fixed as 0.09 cm² using a

non reflective metal mask. The J - V curves and corresponding photovoltaic parameters of the best performing solar cells based on the bare TiO_2 , PABA-treated TiO_2 , and GABA-treated TiO_2 are presented in **Figure 5a**. As expected, the cell performances were significantly affected by the introduction of coupling agents. The efficiency was increased from 13.63% of the bare- TiO_2 device to 15.79% of the GABA-treated cell and 16.8% of the PABA-treated cell. The enhancement of efficiency was majorly due to the great increase of J_{SC} . Similar results have been also reported in the recent work.²² Presumably, the coupling agents linkage of the mesoporous TiO_2 and MAPbI_3 facilitating the electron transport at the TiO_2 /perovskite interface contributed mainly to the increase of photocurrent. In addition, the better coverage of TiO_2 surface by the MAPbI_3 film for the coupling agents treated cells was also beneficial to the improvement of cell performance. Thus, the open circuit voltage (V_{oc}) and fill factor (FF) were also slightly increased. From the statistical efficiency values of the 20 cells, as shown in **Figure 5b**, the average efficiency of the cells was increased from 12.5 to 16.5%. The results are in good agreement with our measurements from the best performing solar cells. And all the data were subject to normal distribution, suggesting our cells have good reproducibility. **Figure 6** summarizes the photovoltaic parameters including efficiency (η), J_{sc} , V_{oc} , and FF of the perovskite solar cells without or with PABA and GABA treatment. Apparently, all of the average parameters in the coupling agents treated cells were superior to those in the cell with bare TiO_2 . Efficiencies of the solar cells without coupling agent treatment were in the range of 12~13% and the efficiency was increased to 15~16.5% in the coupling agents treated cells. Notably, the rigid amino acid PABA treated cells exhibited much higher efficiency and other parameters of J_{sc} , V_{oc} , and FF values are also higher than those of the flexible amino acid GABA treated ones. Therefore, we can conclude that the rigid amino acid can improve the performance of the solar cell more than the flexible one. In

addition, dispersion of efficiency values of the solar cells became smaller after the insertion of the coupling agents between the mesoporous TiO_2 and perovskite, indicating that the fabrication reproducibility of devices was also improved.

On the basis of the results above motioned, a proposed mechanism for the improvements of the MAPbI_3 films and cell performances by the amino acid coupling agents is presented in **Figure 7**. Very similar to the widely used dyes with COO^- as anchoring group in dye-sensitized solar cells, the COO^- group of amino acid can anchor on the TiO_2 film and facilitate the photogenerated electrons transfer from the perovskite layers to the TiO_2 film. Thus, the J_{SC} of the solar cells were greatly improved with the coupling agents treatment. In addition, the NH_3^- group of amino acid can couple with I atom of the perovskite to form hydrogen bonds and the long alkyl chain can improve hydrophobicity of the TiO_2 surface, which also can improve the morphology of the perovskite film and further increase the cell performance. For the PABA treated film, the rigid PABA molecules array neatly on the TiO_2 film owing to $\pi-\pi$ stacking of the benzene rings and act as the nucleation centers for the growth of MAPbI_3 crystalline (**Figure 7a**) and leading to better covered films than those treated by the untidily array of flexible GABA (**Figure 7b**).

3. Conclusion

In summary, we employ two amino acids, PABA and GABA, with similar molecular size as coupling agents to study the influence of molecular rigidity on the perovskite crystallization. Comparison the template effects of the two coupling agents, the rigid PABA improved the quality of perovskite films more obviously by reducing the defects and enhancing the crystalline, thus led to a significant improvement of the photocurrent and efficiency of the solar cells. In addition, the fabrication reproducibility of devices was also improved in the cells with PABA as coupling agent. A high efficiency of 16.80 % was

achieved in the solar cell with PABA treatment. Our results suggested that the solar cell performance could be further improved by carefully selecting the coupling agents to guide the perovskite crystallization.

4. Experimental Section

Fluorine-doped tin oxide-coated (FTO) glass was cleaned by UV-ozone treatment for 30 min, followed by cleaning with acetone and ethanol consecutively. A compact TiO₂ blocking layer was formed by spin-coating of 0.15 M titanium diisopropoxide bis(acetylacetonate) (Aldrich, 75 wt.% in isopropanol) solution in isopropanol (Aldrich, 99.8%) and annealing at 500 °C for 30 min. A porous TiO₂ film was deposited on the compact TiO₂ blocking layer by spin-coating of the TiO₂ paste diluted in terpinol and annealing at 550 °C for 2 h. The porous substrate was dipped respectively in a solution with 5 mM of 4-aminobenzoic acid and 4-aminobutyric acid in ethanol for 2 h to introduce the amine acid template onto the mesoporous TiO₂ films. Then, the sample washed with ethanol to remove the un-chelated residuals and dried under vacuum. To prepare the perovskite precursor solution, lead iodide (PbI₂, Aldrich) and MAI for 1.4 M MAPbI₃ were dissolved in a mixture of *r*-butyrolactone and DMSO (7:3 v/v) with a molar ratio of 1:1 and stirred at 70 °C for 12 h. Then, the devices were annealed at 100 °C for 15 min in the glovebox. Afterward, the sample was covered by 2,2',7,7'-tetrakis-(*N,N*-dimethoxyphenyl-amine)-9,9'-spirobifluorene (spiro-MeOTAD) with sequentially spin-casting at 1000 rpm for 10 s and 3000 rpm for 30 s, respectively. Finally, a 100-nm thick Au electrode was deposited on the top of the sample by thermal evaporation Au particles under ca. 1×10⁻⁶ torr vacuum condition.

For all solar cell devices, the active area was defined as 0.09 cm² by using a non-reflective shadow mask. The current-voltage characteristic curves of the fabricated PSCs were measured under standard AM 1.5 sunlight (100 mW/cm², WXS-90L2, Wacom). The *J-V*

curves were recorded by using a Keithley 2400 sourcemeter and the scanning rate was kept at 25mV/s.

Acknowledgements

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Figures:

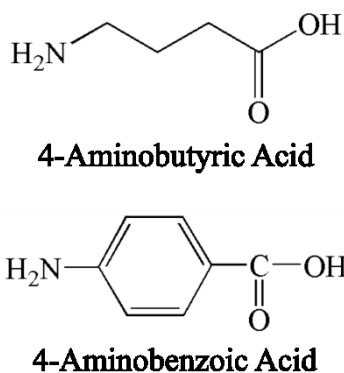


Figure 1. Schematic diagrams of $\text{HOCO-C}_6\text{H}_4\text{-NH}_3^+\Gamma^-$ (PABA) and $\text{HOCO-C}_3\text{H}_6\text{-NH}_3^+\Gamma^-$ (GABA).

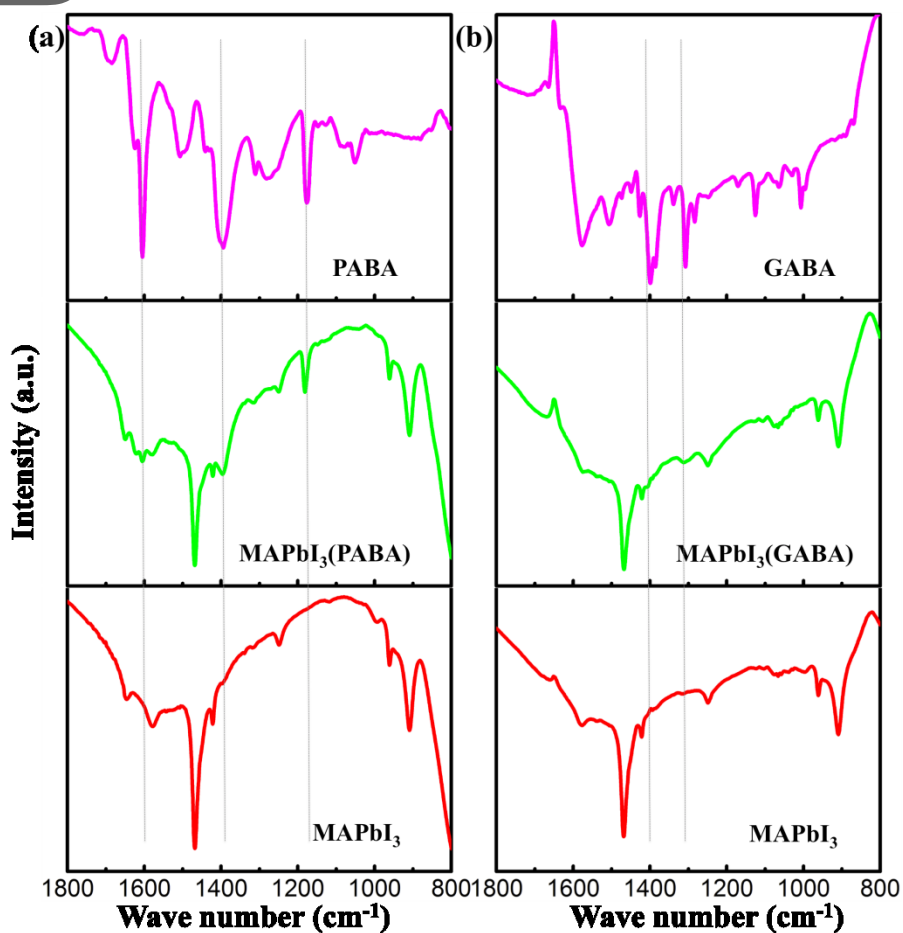


Figure 2. The IR spectra of perovskite layers treated by (a) PABA and (b) GABA.

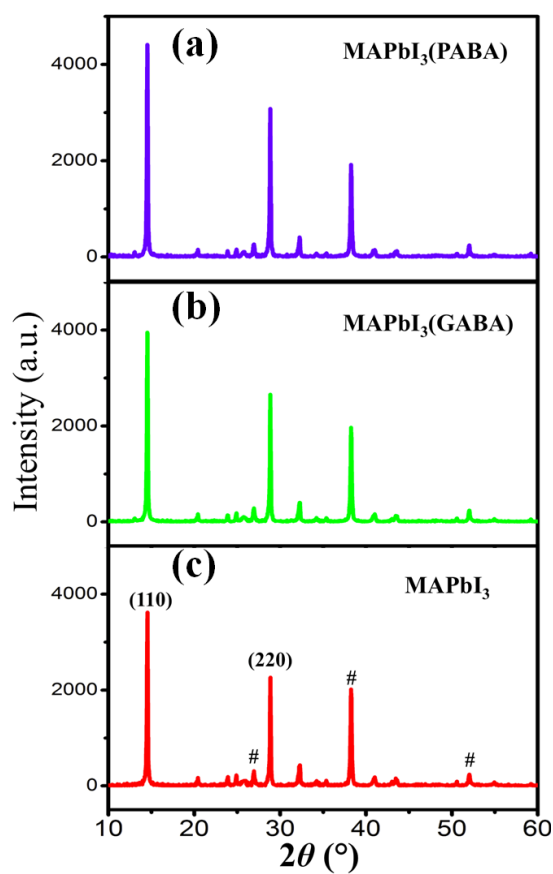


Figure 3. X-ray diffraction patterns of the MAPbI₃ films, (a) PABA-treated TiO₂, (b) GABA-treated TiO₂, and (c) on bare-TiO₂.

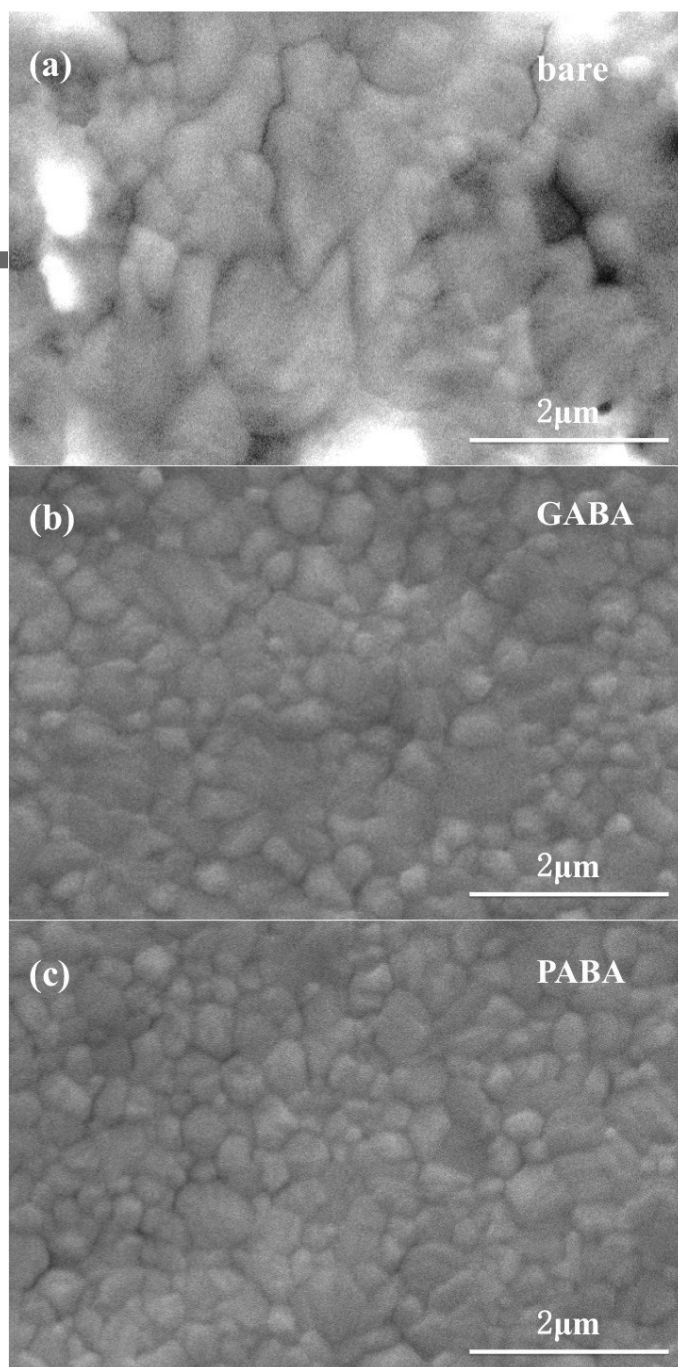


Figure 4. SEM images of the MAPbI₃ films, (a) on bare-TiO₂, (b) on GABA-treated TiO₂, and (c) on PABA-treated TiO₂.

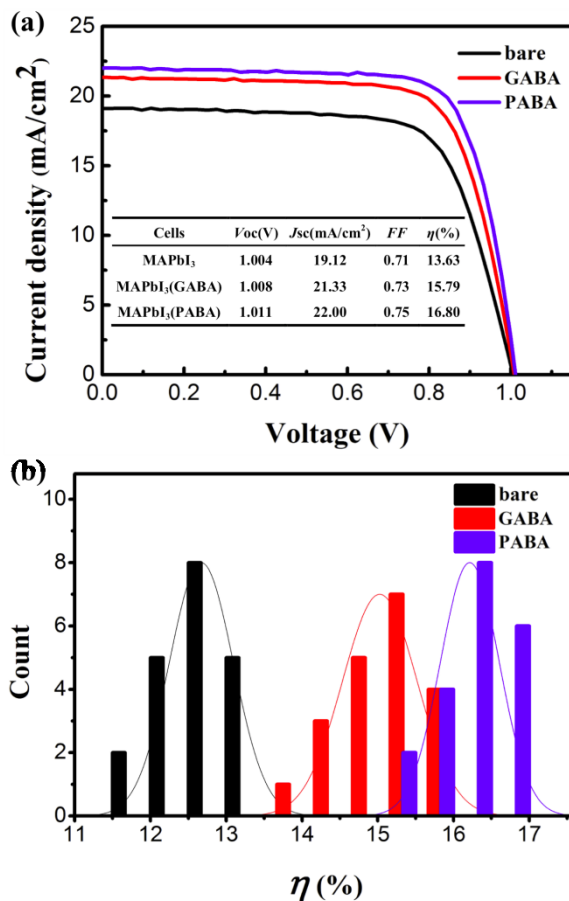


Figure 5. (a) J - V curves of the best perovskite solar cells based on the MAPbI₃ films on bare-TiO₂, GABA-treated TiO₂, and PABA-treated TiO₂; (b) Histograms of photovoltaic efficiencies. The data were collected from 20 perovskite solar cells.

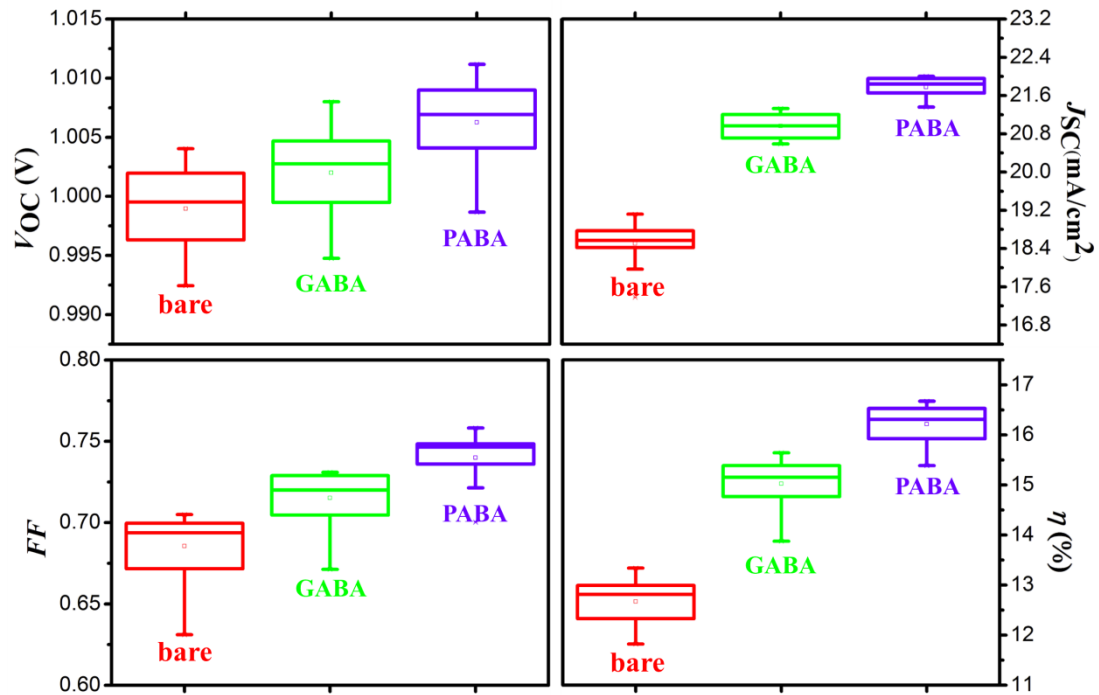


Figure 6. Photovoltaic parameters of the perovskite solar cells. (a) open circuit voltage (V_{OC}), (b) short circuit current (J_{SC}), (c) fill factor (FF), and (d) efficiency (η).

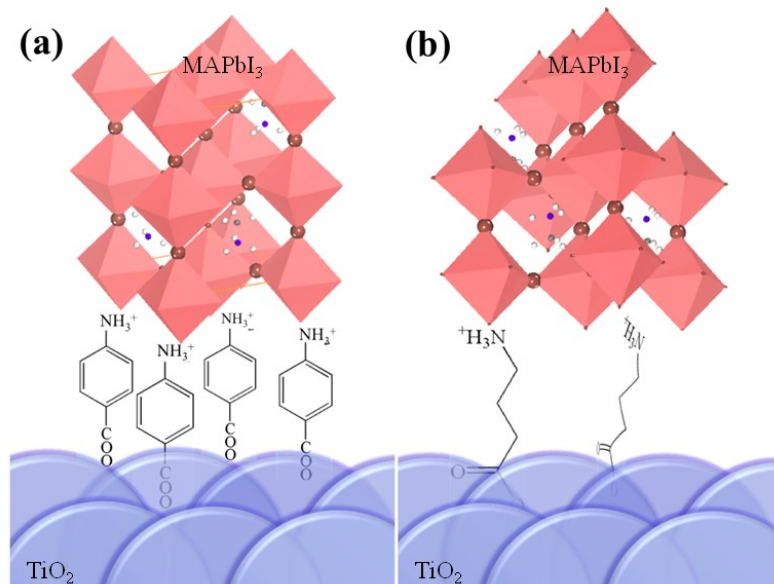


Figure 7. Proposed mechanism of amino acid as template to affect formation of the $MAPbI_3$ films, (a) on PABA-treated TiO_2 , and (b) on GABA-treated TiO_2 .

Rigid amino acid as linker to enhance the crystallinity of $\text{CH}_3\text{NH}_3\text{PbI}_3$ particles

Chenming Zhang, Shufang Zhang*, Xiaoliang Miao, Yanqiang Hu, Leon Staaden, and Guohua Jia*

The molecular rigidity of the organic coupling agents greatly affects the quality of organic-inorganic hybrid perovskite films and the performance of perovskite solar cell is significantly improved by the template effect of rigid 4-aminobenzoic acid.

