

## Perovskite films with reduced interfacial strains via molecular-level flexible interlayer for photovoltaic application

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### Abstract

**Protonated amino silane coupling agents interlayer is exploited on rigid and flexible substrates, which not only set up well-matched growth underlay for perovskite crystal but also serve as structural component of lattice unit in each sides of functional layers leading to less distorted perovskite film with low trap sites. Such strategy results in obvious advance in device performance and stability; meanwhile, the mechanical tolerance in corresponding flexible device is also improved.**

### 1. Introduction

Interface strains and lattice distortion are inevitable issues during perovskite crystallization. Silane coupling agent is a kind of popular connector to enhance the compatibility between inorganic and organic materials in semiconductor devices. Silane coupling agents with low molecular weight organosilicon compound are a kind of widely used interfacial linker materials, which share the formula of Y-R-Si-X<sub>3</sub>, where Y is organic functional group, R is alkylene and X is hydrolyzable group. Generally, Y and X are reactive to inorganic substances and organic substances, by which heterogeneous materials can be flexibly bound. Herein, we adopted a protonated amine silane coupling agent (PASCA-Br) interlayer between TiO<sub>2</sub> and perovskite layers to directionally grasp both of them by forming structural component of lattice unit. The pillowy alkyl ammonium bromide terminals at upper side of interlayer provided well-matched growth sites for perovskite, leading to mitigated interface strain and ensuing lattice distortion, meanwhile, its superior chemical compatibility presented ideal effect on healing under-coordinated Pb atoms and halogen vacancies of bare perovskite crystals. PASCA-Br interlayer also served as a mechanical buffer layer, inducing less cracked perovskite film when bending. The developed molecular-level flexible interlayer provides a promising interfacial engineering for perovskite solar cells and its flexible application.

### 2. General Instructions

PASCA-Br with the protonated alkyl ammonium bromide terminals (R-NH<sub>3</sub>Br) terminal interlayer was grown on TiO<sub>2</sub> film based on chemical bath deposition. Here, we use 3-Aminopropyl triethoxysilane (APTES) to prepare protonated

amine silane coupling agent (PASCA) on TiO<sub>2</sub>, where covalent bond are formed by condensation reaction. To remove redundant products, the substrate was ultrasonic treated in isopropanol. Then, hydrobromic acid (HBr) was used to prepare R-NH<sub>3</sub>Br terminals for PASCA-Br.

To investigate the chemical characteristics and reaction position between TiO<sub>2</sub> and PASCA-Br, X-Ray Photoelectron Spectra (XPS) of different element chemical states were carried out, as shown in Fig.1. Fig. 1a shows the Ti 2p core levels with a shift about 0.2 eV toward higher binding energy after APTES modification, indicating a weak electronic loss characteristic of Ti in TiO<sub>2</sub>. Noticeably, PASCA-Br modification results in a large difference for O 1s spectra (Fig. 1b). For TiO<sub>2</sub> sample, Ti-O bond peak is located around 529.7 eV besides inevitable C=O bond from CO<sub>2</sub> in surrounding environment. In TiO<sub>2</sub>/PASCA-Br sample, a main peak at 532.4 eV ascribed to C-O bond of alkylene in PASCA-Br was observed. Compared to the peak at 530.1 eV corresponding to Ti-O bond of TiO<sub>2</sub>, there is a shift by 0.3 eV toward higher binding energy. Furthermore, Si 2p core levels of pure PASCA-Br and TiO<sub>2</sub>/PASCA-Br films were recorded to explore the chemical states change of PASCA-Br.<sup>[1]</sup> A clear shift by 0.5 eV toward higher binding energy was observed after reacting with TiO<sub>2</sub>, demonstrating a strong chemical bond between Si and TiO<sub>2</sub> (Fig. 1c).

These XPS results reveal that Si could quickly take part in the interaction under the condensation reactions when TiO<sub>2</sub> was dipped in PASCA-Br solution. Generally, perovskite crystals are easily to be passivated by -NH<sub>2</sub> in APTES, working as a Lewis base.<sup>[2]</sup> In present case, R-NH<sub>3</sub>Br terminal would target for bare under-coordinated Pb atoms and compensate for mutilated octahedrons on the surfaces. That means NH<sub>3</sub><sup>+</sup> could partially act as A site role for newly formed perovskite crystals. In a word, the interlayer of PASCA-Br could firmly grasp not only TiO<sub>2</sub> but also perovskite crystals.

Grazing incidence X-ray diffraction (GIXRD) patterns of Cs<sub>0.05</sub>(FA<sub>0.85</sub>MA<sub>0.15</sub>)<sub>0.95</sub>Pb(I<sub>0.85</sub>Br<sub>0.15</sub>)<sub>3</sub> (20 nm) films on TiO<sub>2</sub>, TiO<sub>2</sub>/APTES and TiO<sub>2</sub>/PASCA-Br along in-plane and out-of-plane were measured to compare the change of interface perovskite crystallization. the strain and extendibility of the underlay could be reflected from the perovskite crystallization

according to Williamson-Hall equation.<sup>[3]</sup> Calculated Williamson-Hall plot are shown in Fig.2. After linear fitting, the perovskite lattice strains of perovskite films in in-plane orientation are 1.55% (@TiO<sub>2</sub>), 0.97% (@TiO<sub>2</sub>/APTES) and 0.67% (@TiO<sub>2</sub>/PASCA-Br), and in out-of-plane orientation are 1.47% (@TiO<sub>2</sub>), 1.11% (@TiO<sub>2</sub>/APTES) and 0.73% (@TiO<sub>2</sub>/PASCA-Br), respectively. Since the better connection than common APTES with perovskite crystals, PASCA-Br could suppress the strain at the interface of TiO<sub>2</sub>/perovskite effectively, which is extremely important for perovskite growing at the interface.

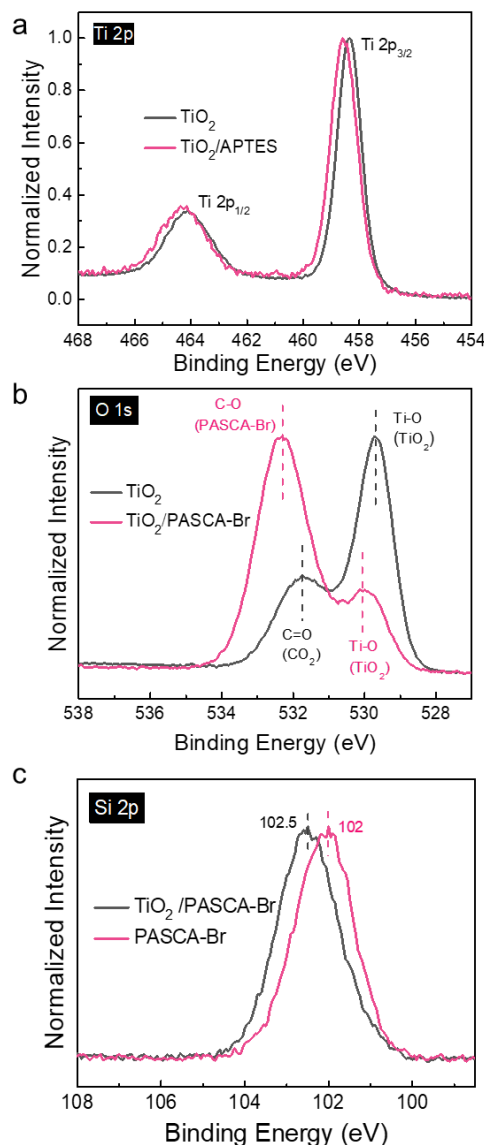


Fig. 1 XPS spectrum of TiO<sub>2</sub> and TiO<sub>2</sub>/PASCA-Br films for (a) Ti 2p and (b) O 1s, TiO<sub>2</sub>/PASCA-Br and PASCA-Br films for (c) Si 2p

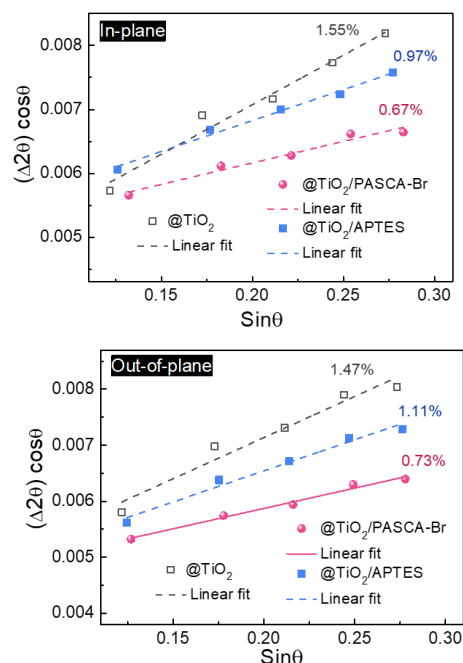


Fig. 2 Calculated lattice strains in in- and out-of-plane orientations.

### 3. Conclusions

PASCA-Br could simultaneously hold TiO<sub>2</sub> and perovskite crystals, and serves as the ideal growth substrate for perovskite. As a result, the perovskite lattice distortion originated from strain stress at TiO<sub>2</sub>/perovskite interface could be relieved, resulting in high quality perovskite crystalline at the interface.

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