**TiO₂ Embedded Structure for Perovskite Solar Cells with Anomalous Grain Growth and Effective Electron Extraction**

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The Scanning electron microscopy (SEM) images of pristine perovskite film and the perovskite films with different amounts of TiO₂ in TiO₂/PbI₂ blend are shown in Fig. S1. From the images, it is clear that the embedded TiO₂ nanoparticles can promote the growth of perovskite grains, observably. The pristine perovskite film presents the poly-crystalline morphology and the average grain size is about 100 nm. In contrast, the perovskite films embedded with TiO₂ nanoparticles (even merely 0.03 wt% in TiO₂/PbI₂ blend) exhibits larger grain size, along with more preferred orientation and more compact morphology.

![Fig. S1](a-d Scanning electron microscopy (SEM) images of (a) the pristine perovskite film; (b), (c) and (d) the TiO₂ embedded perovskite film (corresponding to 0.1 wt%, 0.05 wt% and 0.03 wt% TiO₂ in TiO₂/PbI₂ blend, respectively).]

As shown in Fig. S2, the high-resolution transmission electron microscopy (HRTEM) image of the TiO₂ embedded perovskite is exhibited. Two different interplanar distances are presented, which are consistent to (110) planes of TiO₂ nanoparticles 1 and perovskite grains 2, respectively.
The TiO$_2$ nanoparticles have been embedded in the perovskite grains and have surrounded the perovskite grains. The polycrystalline perovskite grains have grain boundaries with different orientations, which can form many reentrant edges. The reentrant-edge boundaries benefit for the attachment of atoms and have much higher grain boundary energy than other boundaries, which can promote the growth of perovskite grains.

Fig. S2 High-resolution transmission electron microscopy (HRTEM) image of the TiO$_2$ embedded perovskite. A present TiO$_2$ and B present perovskite. As shown in the figure, the lattice spacing of 0.32 nm is consistent to (110) plane of rutile TiO$_2$ and the lattice spacing of 0.62 nm is consistent to (110) plane of perovskite. The reentrant-edge boundaries benefitting for the grain growth, are also exhibited.

The schematic diagrams of the four different process of the time resolved photoluminescence spectroscopy (TRPL) measurement are given in Fig. S3. For comparison, the perovskite film on compact TiO$_2$ is measured from the TiO$_2$ side and the perovskite side, respectively, and show in figure (a): the pristine perovskite film and the TiO$_2$ embedded perovskite film are also characterized as shown in figure (b) and figure (c). When under irradiation, there will be many photo-induced carriers. These carriers can be extracted and transport by TiO$_2$ or be recombined by traps and other carriers.

Fig. S3 Schematic illustrating of the electron extraction and electron transport properties of the perovskite films during the time resolved photoluminescence spectroscopy (TRPL) measurement: (a) TiO$_2$/perovskite film, which was irradiated from the perovskite side and the compact TiO$_2$ side, respectively. (b) Pristine perovskite film and (c) embedded perovskite film, which were irradiated from the perovskite side.
As shown in Fig. S4, the high-resolution transmission electron microscopy (HRTEM) image and the Scanning transmission electron microscopy (STEM) images of the embedded perovskite are displayed. From Fig. S4 (d), it can be observed clearly that the iodine elements are surrounded by titanium, indicating that the embedded TiO$_2$ nanoparticles present in the boundaries of perovskite grains. Moreover, these embedded TiO$_2$ is distributed continuously, forming a passage for transporting the electrons extracted from perovskite, as shown in Fig. S4 (c).

![Fig. S4](image)

**Fig. S4** (a) High-resolution transmission electron microscopy (HRTEM) image of TiO$_2$ embedded perovskite. (b) Scanning transmission electron microscopy (STEM) image of iodine elements. (c) STEM image of titanium elements and (d) STEM image of the iodine and titanium elements of the embedded perovskite grain.

The cross-section SEM images of the standard planar PSC and the TiO$_2$ embedded PSC were shown in Fig. S5. Compared to the cross-section SEM of the standard planar PSC, it can be observed clearly that the cross-section SEM of embedded perovskite film demonstrates that the embedded TiO$_2$ nanoparticles form many electron transport paths, which can conduct the electrons from the perovskite layer to the compact TiO$_2$ layer. Hence, it can be concluded that the electrons injected from perovskite to TiO$_2$ nanoparticles can be transported through the continuous TiO$_2$ nanoparticle network and collected by the compact TiO$_2$ layer.

![Fig. S5](image)

**Fig. S5** Cross-section SEM figures of the PSC with the standard planar structure and with the TiO$_2$ embedded
structure. The schematic illustrating the structure of the TiO$_2$ embedded perovskite solar cells and the networks of the embedded TiO$_2$.

As shown in Fig. S6, the high-resolution transmission electron microscopy (HRTEM) image and the scanning transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (STEM-EDS) of TiO$_2$ embedded perovskite grains are exhibited. From these figures, it is able to see that many perovskite grains stack with each other grains, and the TiO$_2$ nanoparticles are embedded in the boundaries of perovskite grains.

![Fig. S6](image)

**Fig. S6** (a) High-resolution transmission electron microscopy (HRTEM) image and (b) scanning transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (STEM-EDS) of TiO$_2$ embedded perovskite. (c) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and (d) STEM-EDS of the embedded TiO$_2$.

To characterize the chemical change of the perovskite films upon degradation, the X-ray diffraction (XRD) measurement was employed, as shown in Fig. S7 (a, b). In the fresh perovskite films, a series of diffraction peaks can be observed, which can be indexed to the typical diffraction peaks of perovskite and FTO. In the degraded perovskite film, an additional diffraction peak locating at 12.6° can be observed $^3$, which can be indexed to the (001) plane of PbI$_2$, proving that partial of the perovskite is decomposed to PbI$_2$. It is clear that the TiO$_2$ embedded perovskite film shows better stability in the ambient air.
As shown in Fig. S8, XRD pattern and TEM image of the embedded TiO₂ nanoparticle is exhibited. From the XRD pattern, it is clear that the embedded TiO₂ belonging to rutile phase (PDF NO. 21-1276) is well crystallized. From the TEM image, it can be observed clearly that the lattice spacing of 0.32 nm is consistent to (110) plane of rutile TiO₂.

**Fig. S8** XRD pattern of TiO₂ nanoparticles using into the TiO₂ embedded PSCs and TEM image (inside figure) of TiO₂ nanoparticles embedded into the perovskite films.
Reference:

