

## Supporting Information

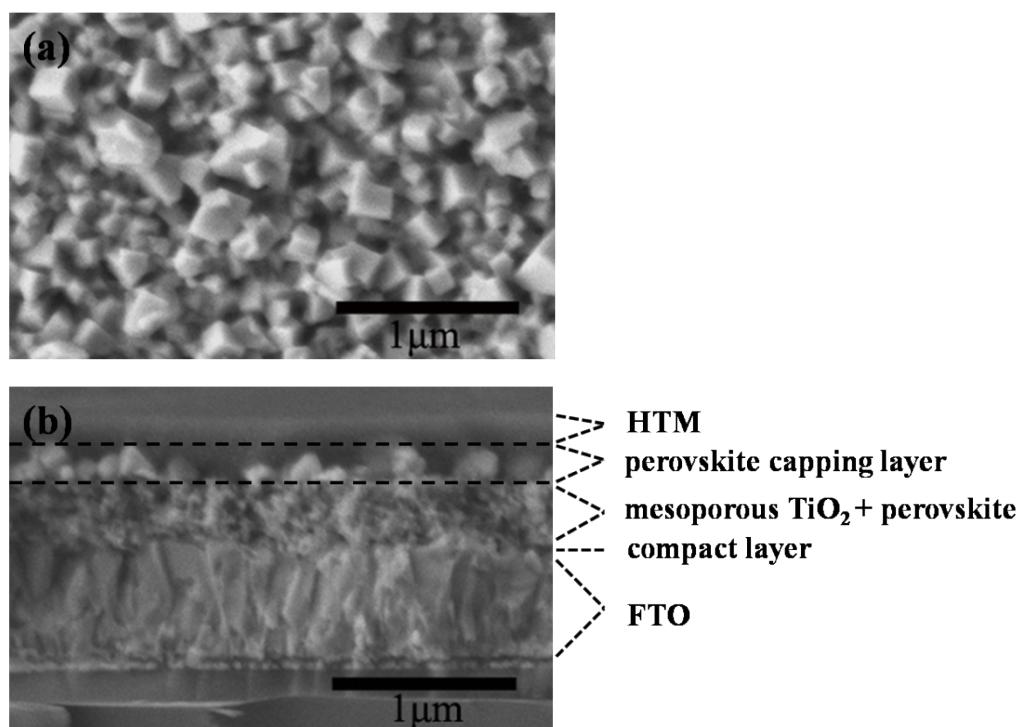
### Multifunctional perovskite capping layers in hybrid solar cells

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#### Cross-sectional SEM image



**Fig. S1** SEM images: (a) the surface sectional SEM image of the perovskite capping layer formed by using PbI<sub>2</sub> solution with a concentration of 463 mg mL<sup>-1</sup> in the sequential deposition method, (b) corresponding cross sectional SEM image of *mp*-TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/Spiro-OMeTAD, with perovskite capping layer between the two long dash lines.

#### The effective dielectric coefficient of TiO<sub>2</sub>/perovskite films

The reflection or scattering of TiO<sub>2</sub>/perovskite films was affected by the effective dielectric coefficient. The effective dielectric coefficients of different TiO<sub>2</sub>/perovskite films in Fig. 1 were measured as shown in Table. S1.

As for the scattering effect of the films in Fig. 1, according to the Mie theory<sup>31</sup>, the extinction cross-section  $C_E$  can be expressed as

$$C_E = C_A + C_S = k_1 \operatorname{Im}(\alpha) + \frac{k_1^4}{6\pi} |\alpha|^2 \quad (1)$$

Where  $C_A$  is the absorption cross section and  $C_S$  is scattering cross section.

$$C_S = \frac{k_1^4}{6\pi} |\alpha|^2 \quad (2)$$

Where  $k_1$  is the wavevector of the incident light in the medium around the perovskite, and  $\alpha$  is the polarizability of perovskite particles.  $\alpha$  can be expressed as:

$$\alpha = 4\pi r^3 \left( 1 - \frac{3\epsilon_1}{\epsilon_m + 2\epsilon_1} \right) \quad (3)$$

Where  $r$  is the diameter of perovskite particles, and  $\epsilon_m$  is the dielectric coefficient of the particles, which represents the effective dielectric coefficient of different  $\text{TiO}_2$ /perovskite films, and  $\epsilon_1$  is the dielectric coefficient of the medium around the perovskite.

According to Eq. 2 and Eq. 3, we get the law

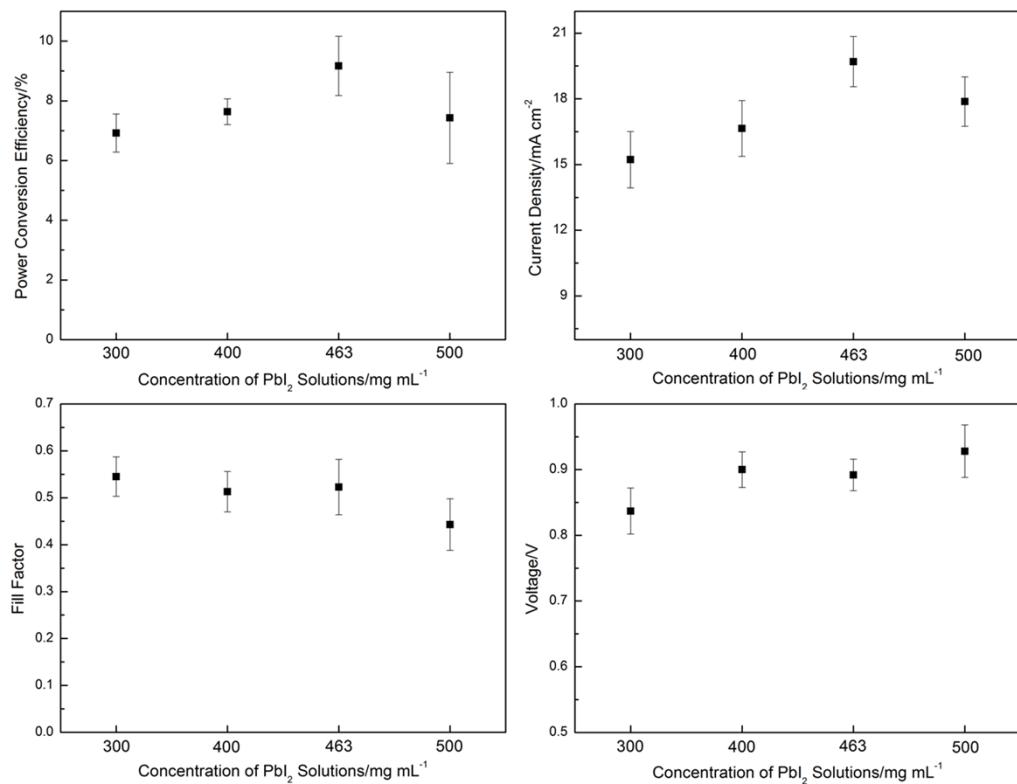
$$C_S \propto r^6 \quad (4)$$

in which the scattering cross section,  $C_S$ , increases as  $r^6$ , and Eq. 3 indicates that  $C_S$  also increases with  $\epsilon_m$ . These indicate that the enhancement of scattering or diffuse reflection of the films in Fig. 4 resulted from both the larger size of perovskite particles and the increased effective dielectric coefficient. Moreover, in the range of 400 mg mL<sup>-1</sup> to 500 mg mL<sup>-1</sup>, the effective dielectric coefficient of  $\text{TiO}_2$ /perovskite films changed slightly, while the size of perovskite particles obviously increased with  $\text{PbI}_2$  concentration. Therefore, both the particle size and the effective dielectric coefficient affect reflectance, and we mainly contribute the enhanced reflectance at higher concentration to the particle size.

**Table S1.** The effective dielectric coefficient of *mp*- $\text{TiO}_2$ /perovskite films.

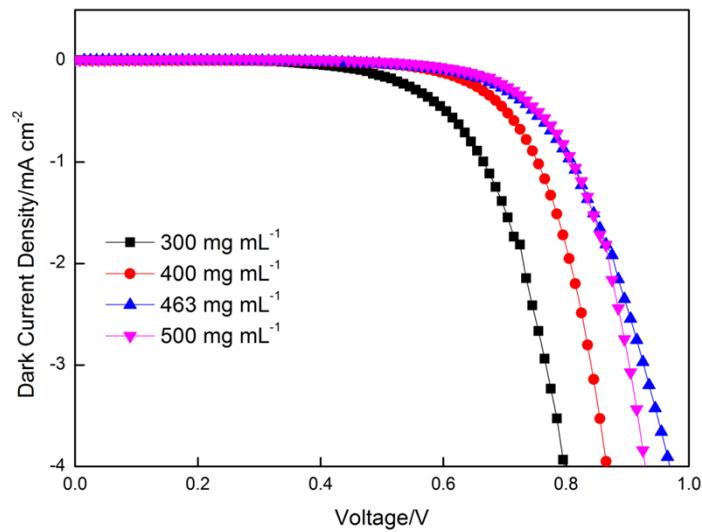
$C(\text{PbI}_2)/\text{mg mL}^{-1}$	300	400	463	500
$\epsilon_m$	29.943	43.678	45.991	47.205

## Performance parameters extracted from a batch of solar cells



**Fig. S2** Performance parameters extracted from current density-voltage data for a batch of solar cells with the four  $\text{PbI}_2$  concentrations.

## $J$ - $V$ curves in the dark condition



**Fig. S3**  $J$ - $V$  curves of solar cells in the dark condition.

As the concentration of  $\text{PbI}_2$  solutions increased from  $300 \text{ mg mL}^{-1}$  to  $463 \text{ mg mL}^{-1}$ , the charge recombination was reduced due to the increased coverage of perovskite capping layers on *mp*- $\text{TiO}_2$  films. However, when the concentration was up to  $500 \text{ mg mL}^{-1}$ , the recombination increased and we contributed it to the small amount of voids in the capping layers shown in the SEM image (Fig. 1(d)), which increased the possibility of charge recombination caused by the direct contact of spiro-OMeTAD and  $\text{TiO}_2$ .