Supporting Information

Electrical characterization of TiO₂/CH₃NH₃PbI₃ heterojunction

solar cells

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Figure S1. X-ray diffraction pattern of a typical TiO₂ film prepared by solvothermal reaction, sintered at 550 °C.

The crystallinity and growth orientation of TiO₂ films prepared by solvothermal reaction were examined by powder X-ray diffraction (XRD) at room temperature with a Bruker D8-Advance diffractometer, employing Cu K α radiation ($\lambda = 1.5418$ Å) in the range of 10° to 80°. Figure S1 shows a typical XRD pattern of TiO₂ film prepared by solvothermal reaction. It is found that the sample has seven diffraction peaks at 2 θ values of 27.58°, 36.30°, 37.86°, 41.30°, 54.42°, 62.86°, and 65.66° can be readily

attributed to the (110), (101), (111), (211), (002), and (211) planes of rutile TiO₂ (JCPDS Card No. 21-1276), respectively, while the peak at 37.86° can be attributed to the (004) plane of anatase TiO₂ (JCPDS Card No. 21-1272). No peaks of impurities were observed. This suggests that rutile TiO₂ and anatase TiO₂ phases coexist in the TiO₂ film deposited on the FTO substrate prepared by solvothermal reaction. By comparison, the as-prepared TiO₂ film is dominated by rutile phase. Furthermore, the XRD pattern for the as-prepared TiO₂ film is different in the relative intensities of the (110) and (002) peaks from rutile TiO₂ (JCPDS Card No. 21-1276). The intensity of the (002) peak is the strongest in all peaks, rather than the (110) peak of rutile TiO₂ is highly oriented along the (002) plane on FTO substrate during the solvothermal reaction. Such highly oriented rutile TiO₂ films with strong (002) diffraction peak are similar to the oriented, single-crystalline rutile TiO₂ nanorod films prepared by a hydrothermal method. (Bin Liu and Eray S. Aydil, J. Am. Chem. Soc. 2009, 131, 3985–3990)



Figure S2. Typical Nyquist plots of a solar cell based on TiO₂/CH₃NH₃PbI₃. Filled squares, fresh cell; open triangles, cell stored 15 days in air ambient. The curves show

theoretical fits using the equivalent circuits shown in the inset.

Figure S2 shows typical Nyquist plots of the freshly prepared cell and its degraded cell stored 15 days in air ambient. From Figure S2, it can be seen that the diameter of semicircle of the degraded cell is much larger than that of the freshly prepared cell. Nyquist plots of fresh and degraded devices were fitted by the equivalent circuit shown as the inset in Figure S2. The fitting curves are shown in Figure S2 as solid curves together with the experimental data denoted as symbols. The parameters determined by the fitting of the experimental data are summarized in Table S1. In this equivalent circuit, series resistance (R_s) represents the Ohmic resistance including the electrodes and bulk resistance in the cell. Generally, V_{oc} would be increased due to the increase of R_s . On the other hand, R_p is dominated by the interface charge transport process. Larger R_p represents less recombination in charge transport process, which can lead to improved collection of charge carriers at open circuit. Thus higher V_{oc} value can be obtained. However, increasing with the resistance, the photocurrents and fill factor may be reduced.

equivalent circuit model.Device $R_s(\Omega \, \mathrm{cm}^2)$ $R_p(\Omega \, \mathrm{cm}^2)$ CPE-T(F/cm^2)CPE-PFresh cell7.73294e-70.853Degraded for 15 days8.012405e-70.784

Table S1. Parameters employed for the fitting of the impedance spectra by use of an