

Supplementary information

Yttrium-substituted Nanocrystalline TiO₂ Photoanode for perovskite Based Heterojunction Solar Cells

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Synthesis of TiO₂ and 0.5%Y-TiO₂ pastes:

The starting materials for the preparation of TiO₂ colloid is titanium isopropoxide and acetic acid. 0.2 mol of titanium isopropoxide (58.6 g in 100 ml water) is mixed with 0.2 mol of acetic acid (accounts for 12 g). Acetic acid is slowly added to the titanium isopropoxide under constant stirring. For Y substituted TiO₂, YCl₃ (99.9%, Aldrich) was used as a precursor and 0.5 atomic % of YCl₃ was dissolved in ethanol and additionally added to the titanium isopropoxide + acetic acid mixture. This mixture is stirred for 15 minutes with the beaker covered with a sheet of paraffin wax. This is then, transferred to a 1000 ml conical flask containing 350 ml of water coupled with vigorous stirring. A white precipitate is formed at the beginning but it is dispersed in the water after 1 hour of constant stirring. 4 ml of concentrated HNO₃ (65%) is then added to the white solution. The mixture is heated to 78°C with a ramp time of 45 min

and then this temperature is maintained for a period of 90 min till all the aggregates are dispersed uniformly inside the solution. The good dispersion or complete peptization of particles are indicated the by the change of white colored solution to light blue. The resultant solution is distilled in rotatory vapour (rotovap) instrument to remove the isopropanol, which is formed as a byproduct, and water. The pressure is varied from 200 torr to 90 torr, with the rotovap bath temperature maintained at 50°C. The distillation is continued until the total mass of the suspension reach 150 g. The hydrothermal growth of this suspension is achieved by autoclaving the resultant colloid at 250 °C for 12 hours. 1 ml of concentrated HNO₃ (65%), is then added to autoclaved colloid. This is further dispersed using a titanium probed ultrasonicator at a frequency of 30 pulses for every 2 seconds and is repeated 3 times with alternate stirring. The suspension is concentrated in rotovap, till 20 wt % of TiO₂ is reached. The concentrated colloid contains roughly 16 g of TiO₂ in the 80 g suspension. The resultant colloid is centrifuged thrice in ethanol (twice the volume of colloid) at 4500 rpm for 32 minutes, to remove water and nitric acid. The centrifuged TiO₂ accounts for 18 weight % in the suspension. The centrifugate is stored to prepare paste for electrode preparation as described in (*Thin solid Films*, 2008, **516**, 4613).

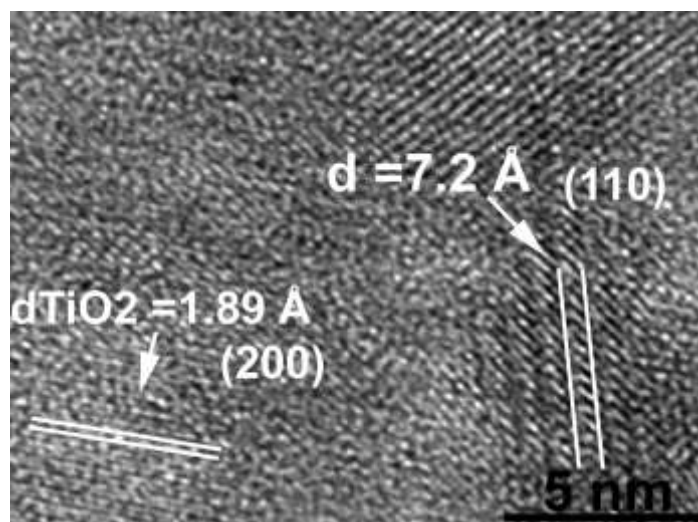


Figure S1 | HRTEM analysis of TiO₂/CH₃NH₃PbI₃ electrode. HRTEM micrograph of dark colour individual nanoparticles deposited on TiO₂.

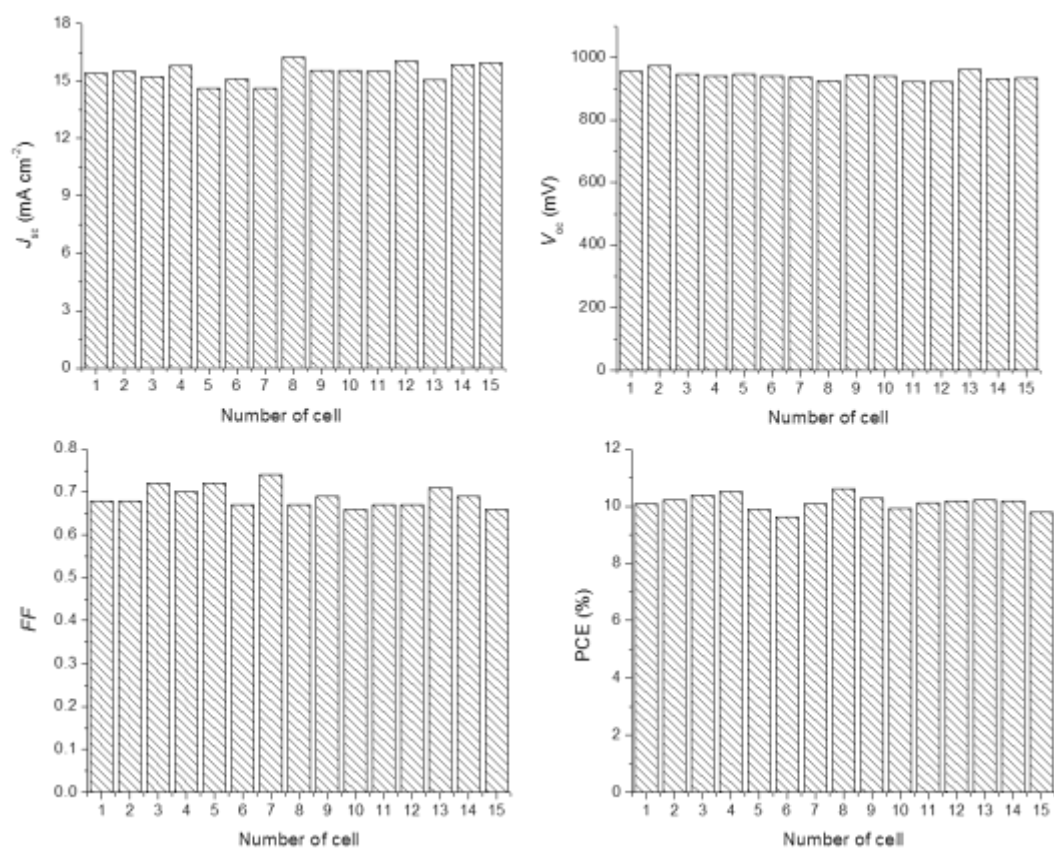


Figure S2 | Histogram plots of solar cell performance parameters: J_{sc} , V_{oc} , FF , and PCE for 15 cells based on TiO_2 .

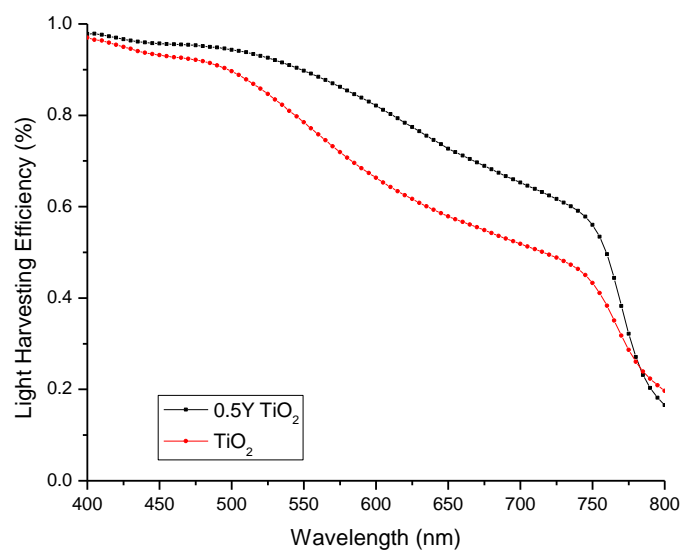


Figure S3 | The light harvesting efficiency spectra of the devices based on 0.5%Y-TiO₂ (black) and TiO₂ (red).

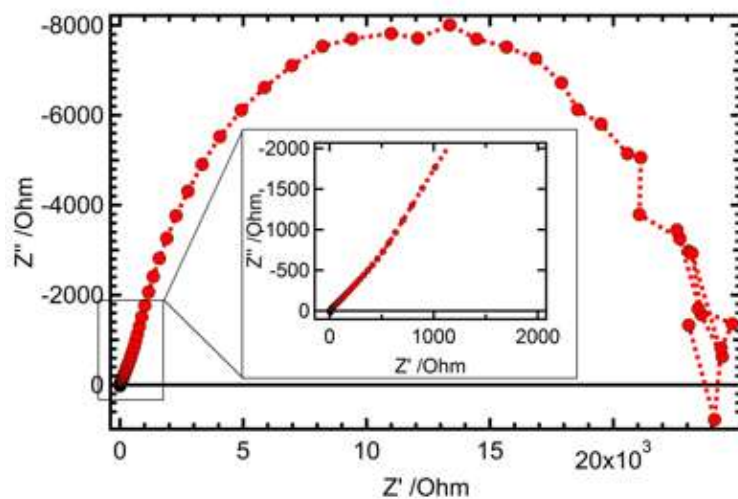


Figure S4 | Impedance spectroscopy results. Nyquist plot of the device without Y at 500mV forward bias. The inset shows the high to intermediate frequency response with the 45° transmission line. The low semicircle represents the charge transfer at the mesoporous TiO₂ to the HTM and its chemical capacitance.