Electronic Supplementary Information:

Polystyrene nanoparticles-templated hollow titania nanosphere monolayers as ordered scaffolds

V. Robbiano^a, *G. M. Paternò^a*, *G. F. Cotella^a*, *T. Fiore^b*, *M. Dianetti^c*, *M. Scopelliti^b*, *F. Brunetti^c*, *B. Pignataro^{bd}*, and *F. Cacialli^{a*}*

^a Department of Physics and Astronomy and London Centre for Nanotechnology, University College London, WC1E 6BT, United Kingdom

^b Dipartimento di Fisica e Chimica (DiFC), Università degli Studi di Palermo, V.le delle Scienze, Ed. 17 –
90128, Palermo, Italy

[°]CHOSE Centre for Hybrid and Organic Solar Energy, Department of Electronic Engineering, University of Rome Tor Vergata, Via del Politecnico 1, 00133 Rome, Italy

^d Aten Center, Università degli Studi di Palermo, V.le delle Scienze, Ed. 18 - 90128 Palermo, Italy

* Corresponding author: f.cacialli@ucl.ac.uk

AFM images



Figure SI_1. Higher magnification AFM images of the titania scaffold prepared from the microspheres with a diameter of 370 nm. The morphology of the original PS microspheres is reproduced well. The scale-bar is 1µm.



Figure SI_2: Higher magnification AFM images of the titania scaffold prepared from the microspheres with a diameter of 430 nm. The morphology of the original PS microspheres is reproduced well. The scale-bar is $1\mu m$.



Figure SI_3: Line profiles obtained from the AFM images of the pristine polystyrene nanospheres monolayers made with beads with a diameter of 370 nm (a) and 430 nm (b) and from the titania scaffold prepared from the nanospheres with a diameter of 370 nm (c) and 430 nm (d). The surface roughness of the titania replica of the nanospheres is comparable to the one of the pristine ones.

SEM images



Figure SI_4: (a) and (b) FIB-milled SEM micrograph in two different area of the titania hollow spheres monolayer detailing the internal structure and the nanospheres walls.

Perovskite morphology



Figure SI_5: AFM (tapping mode) images of the perovskite layer synthesized onto the nanostructured titania starting from (a) spheres having a diameter of 370 nm, (b) the mesoporous titania layer (the arrows indicate the mesoporous titania layer underneath that is not been fully covered by the perovskite layer) and (c) on compact titania layer. Scale-bars are 4 μ m.

XRD spectra



Figure SI_6: XRD spectra of the perovskite layer sintered onto FTO/cTiO2 (black line), FTO/cTiO2/mesoporous (red line), and FTO/cTiO2/nanostructure (blue line for the microspheres with 370 nm diameter, green line for the microspheres with 430 nm diameter) substrates. Broader peaks (FWHM inset) for the perovskite prepared onto the mesoporous and nanostructured films. Principal perovskite peaks: 2 theta= $14.2 \circ (110)$, $28.4 \circ (220)$.

Kelvin Probe measurements

| sample | WF (eV) |
|-----------------------------|---------|
| 430drop | 4.482 |
| 370drop | 4.495 |
| c-TiO ₂ | 4.208 |
| Mesoporous TiO ₂ | 4.448 |

Figure SI_7: Work function (WF) measurements of the various TiO₂ ETL layers.

J-V characteristics



Figure SI_8: J-V curves of the devices reported in figures 4 under illumination (darker lines) and in dark (lighter lines).



Figure SI_9: Hysteresis measurement of FTO/c-TiO2/370nm drop/Perovskite/Spiro-OmeTAD/Au.





Figure SI_10: One-diode model fits (R²>0.97) for each titania scaffolds.



Figure SI_11: Series resistance (R_s) and shunt resistance (R_{sh}) for devices obtained from the fit of the current density – voltage curve.