Supporting Information

In-Situ processed gold nanoparticle embedded TiO$_2$ nanofibers for efficient plasmonic perovskite solar cells exceeding 14% conversion efficiency

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S1 Characterizations:

The top-surface and cross-sectional images were recorded by a field emission scanning electron microscope (FESEM; S-4700, Hitachi). Transmission electron microscopy (TEM) micrographs, selected area electron diffraction (SAED) patter and high-resolution transmission electron microscopy (HRTEM) images were obtained by TECNAI F20 Philips operated at 200 KV. The TEM sample was prepared by drop casting of ethanolic dispersion of sample onto a carbon coated Cu grid. X-ray diffraction (XRD) measurements were carried out using a D/MAX Uitima IIIXRD spectrometer (Rigaku, Japan) with Cu K line of 1.5410 Å. The elemental information regarding the deposited samples were analyzed using an X-ray photoelectron spectrometer (XPS) (VG Multilab 2000-Thermo Scientific, USA, K-Alpha) with a multi-channel detector, which can endure high photonic energies from 0.1 to 3 keV.

The open circuit voltage decay (OCVD) measurements were obtained Iviumstat work station (Ivium Technologies B.V., Eindhoven, The Netherlands). The cells were illuminated using a solar simulator at AM 1.5 G for 10 s, where the light intensity was adjusted with an NREL-calibrated Si solar cell with a KG-5 filter to 1 sun intensity (100 mW cm$^{-2}$). OCVD method was performed on a photovoltaic device by abruptly turning off the illumination and recording the Voc decay. The IPCE spectra were measured as a function of wavelength from 300 to 1100 nm on the basis of a Spectral Products DK240 monochromator. Impedance spectroscopy (IS) was conducted using Iviumstat (Ivium Technologies B.V., Eindhoven, the Netherlands) at an open-circuit potential at frequencies ranging from $10^{-1}$ to $10^{5}$ Hz with an AC amplitude of 10 mV. The amplitude of the modulation voltage was 10 mV. Z-view2.8d (Scribner Associates) was used to fit the EIS spectra to the equivalent circuit based on the transmission line model. The DC bias potential was applied in 0.05V step intervals. Photoluminescence measurements were carried out on a PL mapper (Accent Opt. Tech. UK, Model:RPM2000, 532nm ND-YAG laser excitation). Time-resolved
photoluminescence (PL) decay transients were measured at 750±20nm using excitation with a 470nm light pulse at a frequency of 5MHz from the Spectrophotometer F-7000. Optical absorption measurements were carried out on a UV-vis spectrophotometer (Varian, CARY, 300 Conc.) in the 280-900 nm wavelength range.
We have optimized our perovskite synthesis recipe with respect to washing MAI with diethyl ether, recrystallize process and drying temperature. Our results indicate that the CH₃NH₃PbI₃ dried at 90°C shows good photo-conversion efficiency. Double wash MAI was used for perovskite synthesis.
Figure S1(b) XRD pattern of optimized CH$_3$NH$_3$PbI$_3$ sample deposited on glass substrate. The MAI was prepared and recrystallize three times using diethyl ether.

The XRD results reveal CH$_3$NH$_3$PbI$_3$ characteristic peaks at 14.36, 28.61, 32.081, and 40.648 corresponding to the (110), (220), (310) and (224) planes of CH$_3$NH$_3$PbI$_3$, respectively, as shown in Figure S1(b). Our calculated lattice parameters for CH$_3$NH$_3$PbI$_3$ with a tetragonal unit cell are $a=b=8.879\,\text{Å}$ and $c=12.558\,\text{Å}$ which is in agreement with previous reports $a=b=8.883\,\text{Å}$ and $c=12.677\,\text{Å}$ [1, 2, 3].

References:
**Figure S2** (a) Plan view of STEM micrographs of Au@TiO$_2$/CH$_3$NH$_3$PbI$_3$ nanofibers and EDS mapping of (b) titanium, (c) oxygen, (c) gold (d) lead and (f) iodine elements.

**Figure S2** shows high resolution TEM micrographs of TiO$_2$ nanoparticle loaded with perovskite CH$_3$NH$_3$PbI$_3$ deposited, along with pure CH$_3$NH$_3$PbI$_3$ particles obtained by drying the $\gamma$-butyrolactone solution and bare TiO$_2$ nanoparticles. From STEM image it is clear that, the perovskite CH$_3$NH$_3$PbI$_3$ are homogeneously distributed onto nanoparticulate TiO$_2$ nanofiber surface. The nanocrystalline CH$_3$NH$_3$PbI$_3$ with $\sim$8-10 nm has been deposited on TiO$_2$ surface. Moreover, perovskite nanoparticles are well adsorbed on TiO$_2$ surface as can be seen from the wide view of TEM in inset of Fig. 1(b), which is consistent with the EDS elemental analysis.
Figure S3 Morphological and topological characterization of Au@TiO$_2$ nanofibers. (a) FESEM image of synthesized Au@TiO$_2$ nanofibers (b) TEM micrograph of the Au@TiO$_2$ nanofibers (c) higher magnified image of Au@TiO$_2$ nanofiber at selected area (d) SAED pattern of Au@TiO$_2$ sample (e) & (f) higher magnified TEM micrographs of TiO$_2$ nanofibers and single Au nanoparticle.
Figure S4 HRTEM characterization of perovskite deposited Au@TiO$_2$ nanofibers. (a) TEM image of single Au@TiO$_2$ nanofiber deposited with perovskite (b) (c) and (d) TEM micrograph of the perovskite deposited Au@TiO$_2$ nanofiber as different magnifications (e) higher magnified image of single Au nanoparticle (e) higher magnified TEM image of selected perovskite area. (g) HRTEM image of selected area showing highly crystalline TiO$_2$ as well as perovskite.
**Figure S5** Nitrogen adsorption–desorption isotherms of the TiO$_2$ and Au@TiO$_2$ nanofibers.
Figure S5 FESEM image of CH$_3$NH$_3$PbI$_3$ thin film. Inset photograph shows the prepared fresh CH$_3$NH$_3$PbI$_3$ solution in $\gamma$-butyrolactone.
Figure S7 FESEM image of (CH$_3$NH$_3$)$_2$PbI$_3$ thin film after coating of HTM layer showing islands are covered onto perovskite/Au@TiO$_2$ surface.
Figure S8. Compositional analysis of Au@TiO$_2$ nanofiber based perovskite device: (a) Cross-sectional fieldemissionscanning electron micrograph (FESEM) of a fabricated device. (b) Energydispersive x-ray (EDX) spectroscopy analysis with elemental mapping of (c) titanium, (d) lead (e)iodine (f) tin, (h)carbon (Please note that Sn element is present may be due to FTO substrate)
Figure S9 Compositional analysis of perovskite thin films (a) survey spectra of TiO$_2$ nanofibers/perovskite and Au@TiO$_2$ nanofibers/perovskite thin films (b) core level spectra of Ti(2p) (c) core level spectra of O(1s) (d) Pb(4f) core level spectra (f) I(3d) core level spectra (g) valence band spectra of CH$_3$NH$_3$PbI$_3$ thin films deposited on TiO$_2$ and Au@TiO$_2$ nanofibers. (Pink line perovskite/TiO$_2$ nanofiber, Violet line perovskite/Au@TiO$_2$ nanofibers)
Figure S10 (a) J-V curves measured for perovskite device measured at a simulated AM 1.5G solar irradiation of 100mWcm$^{-2}$.

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Figure S10 (b) J-V curves measured for perovskite device measured at a simulated AM 1.5G solar irradiation of 100mWcm$^{-2}$. Nearly 58nm Au NPs initially prepared and then added in mp-TiO$_2$ pastel.

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**Figure S11** Impedance spectroscopy measurements: Dark current during IS measurements of TiO$_2$ nanofibers (pink color) and Au@TiO$_2$ nanofiber based perovskite devices.
Figure S12. Photograph of synthesized bare TiO$_2$ nanofibers and Au decorated TiO$_2$ nanofibers.

Figure S13. Weight loss as a function of temperature for the as deposited TiO$_2$ and Au@TiO$_2$ nanofibers. Thermogravimetric analysis (TGA) was performed at rate of 10$^\circ$C/min under nitrogen atmosphere (Flow rate: 50ml/min).
Figure S14 XRD patterns of bare TiO$_2$ nanofibers and Au@TiO$_2$ nanofibers.
Figure S15 Morphological and topological characterization of TiO$_2$ nanofiber
(a) FESEM image of synthesized TiO$_2$ nanofibers (b) TEM micrograph of the single nanofiber (c) The higher magnified image (c) HRTEM micrograph of the TiO$_2$ nanofibers with lattice planes.

Figure S16 (a) Plan view of SEM micrographs of Au@TiO$_2$ nanofibers and EDS mapping of (b) titanium, (c) oxygen and (d) gold element mapping.
Figure S17. Weight loss as a function of temperature for the mixed MAI and PbI₂ powder. Thermogravimetric analysis (TGA) was performed at rate of 10°C/min under nitrogen atmosphere (Flow rate: 50ml/min).
Figure S18 Morphological and topological characterization of mp-TiO$_2$ based perovskite solar cells. (a) Cross-sectional FESEM image of fabricated perovskite solar cell device. (b) The higher magnified image of perovskite coated mp-TiO$_2$ of selected area. (c) TEM micrograph of the perovskite (CH$_3$NH$_3$)PbI$_3$ deposited on ms-TiO$_2$ nanoparticles. (d) Highly magnified TEM image of CH$_3$NH$_3$PbI$_3$ coated TiO$_2$ nanoparticles. (e) SAED pattern of TiO$_2$ nanoparticles. (f) Highly magnified TEM image. (g) HRTEM image of CH$_3$NH$_3$PbI$_3$. (h) SAED pattern of CH$_3$NH$_3$PbI$_3$. 

![Image of perovskite solar cell device and TEM micrographs](image.png)
**Figure S19** (a) Plan view of TSEM micrographs of P25/CH$_3$NH$_3$PbI$_3$ and EDS mapping of (b) titanium, (c) lead and (d) iodine element.

**Figure S20** EDS spectrum of selected area of Au@TiO$_2$ (commercial paste) based perovskite device
Figure S 21(a) XRD pattern of mp-TiO$_2$ sample deposited on to glass substrate.

Figure S 21(b) XRD pattern of mp-TiO$_2$ sample deposited on to FTO substrate. The peaks denoted by star (*) symbol are originated from FTO substrate.
Table S1 Optimization of Spiro-MeOTAD HTM layer and respect to their device performance of bare TiO$_2$ nanofiber based and Au@TiO$_2$ nanofiber based devices. Thickness of HTM were optimized by using spin coating rate.

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<th>TiO$_2$ Nanofibers</th>
<th>Thickness (~nm)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>Au@TiO$_2$ Nanofibers</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
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