Supporting Information

Arrays of Spherical Nanostructured Oxide Particles for Photon Management Enhancement in Photovoltaic Devices

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Experimental Section

Materials preparation

Materials: N, N-Dimethylformamide (DMF, 99%), HI (57% wt%), and $TiCl_4$ were gained from Alfa Aesar. Cesium iodide (CsI, ≥99.99%), 2,2′,7,7′-tetrakis (N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (Spiro-OMeTAD), lead (II) iodide (PbI_2, >99.99%), lithium bis(tri-fluoromethanesulfonyl)imide (Li-TFSI), tert-butylpyridine (TBP) and tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine) cobalt(III) tri[bis(trifluoromethane)sulfonimide] (FK209) were acquired from Xi'an Polymer Light Company. Aluminum oxide (Al_2O_3, α-phase, 200 nm, 99.99%), Zirconium dioxide (ZrO_2, 200 nm, 99.99%), and Silicon dioxide (SiO_2, 200 nm, 99.99%) were purchased from Alfa Aesar. We did not further purification of the materials before we used them.

DMAI intermediate Synthesis: Under the condition of an ice bath (0°C), DMF (25 mL) was gradually added dropwise to the HI (100 mL) solution, and stirred at 400 rpm for 6 hours (h). After the stirring is completed, use the rotary steaming apparatus to collect the precipitate at a temperature of about 90°C. Following that, it was dissolved in ethanol repeatedly and precipitated with anhydrous ether to obtain a white sample. Then heated in a vacuum oven at 60°C overnight to form DMAI powder.

$CsPbI_3$ film preparation: The precursor solution was formed by dissolving DMAI (0.1661 g), PbI_2 (0.2766 g) and CsI (0.156 g) in 1 mL DMF solution under continuous stirring for 2 h.

HTL Solution Preparation: A solution was prepared by dissolving Spiro-OMeTAD (145 mg), 22 μL Li-TFSI solution (520 mg Li-TFSI in 1 mL acetonitrile), 36 μL TBP, and 36 μL FK209 solution (300 mg FK209 in 1 mL acetonitrile) in 1 mL of CB solution.

Device fabrication preparation

Preparation of TiO_2-blocking layer: The purchased FTO glass was ultrasonically cleaned with ethanol and isopropanol for 30 minutes (min), then dried with dry air, and treated with O_2 plasma for 10 min. Afterward, the FTO glasses were immersed in 4.5 mL $TiCl_4$ aqueous solution at 70°C for 60 min and washed with distilled water and ethanol. The compact TiO_2 film was formed after annealing at 200°C for 30 min. To prepare SNOPs (Al_2O_3, ZrO_2, SiO_2) doped TiO_2 layer, first, dissolve the SNOPs in cyclohexane, followed spin-coat on clean FTO glass, and then continue the above steps.

Growth of the $CsPbI_3$ film: The perovskite precursor solution was coated on TiO_2 substrate by one-step spin-coating method at 1000 rpm for 10 s and 3000 rpm for 35 s, respectively. The final films were formed after annealing at 210°C for ~10 minutes. To prepare SNOPs (Al_2O_3, ZrO_2, SiO_2) doped PVK layer, we dissolve 0.1mg/mL of SNOPs in the prepared precursor solution and then continue the above steps.

Assembly of the solar cells: The hole transport layer (Spiro-OMeTAD) was coated on perovskite film by spin coating at 5000 rpm for 35 s. To prepare Spiro mixed with SNOPs (Al_2O_3, ZrO_2, SiO_2), we dissolve 0.1 mg of SNOPs directly into Spiro. Finally, thermally evaporated thick gold (~ 80 nm) was used as top electrodes (devices area: 0.09 cm^2).

Characterization Section:

Absorbance and PL spectra: Absorbance results were collected by FLS920T using the slowest scanning rate with one-second integration and a 2 nm slit width. The PL spectra were measured using a PicoQuant FluoTime 300.

XRD: The X-ray diffraction (XRD) patterns were characterized by the Shimadzu XRD-6000 X-ray diffractometer with a Cu Kα (λ = 0.1541 nm).

SEM: The surface morphology of No addition and add SNOPs (Al_2O_3, ZrO_2, SiO_2) was measured by SEM using the Hitachi S-4800 scanning electron microscope.

J-V, *EQE*, and *Steady measurement*: The *J-V* and Steady measurements were performed via the solar simulator (SS-F5-3A, Enlitech) along with AM 1.5G spectra whose intensity was calibrated by the certified standard silicon solar cell (SRC-2020, Enlitech) at 100 mW/cm^2. This used reverse scan mode (from V_{OC} to J_{SC}) and forward scan mode (from V_{OC} to J_{SC}) with a scan rate of 30 mV/s. The external quantum efficiency (EQE) data were obtained by using the solar-cell spectral-response measurement system (QE-R3011, Enlitech).

Simulation Section:

The simulation mainly targets the light field. All the simulations are calculated with the finite-difference time-domain (FDTD) method. Periodic boundary conditions are used to simulate the infinite structural distributions. For each simulation, planar waves with different polarizations are incident to the device.

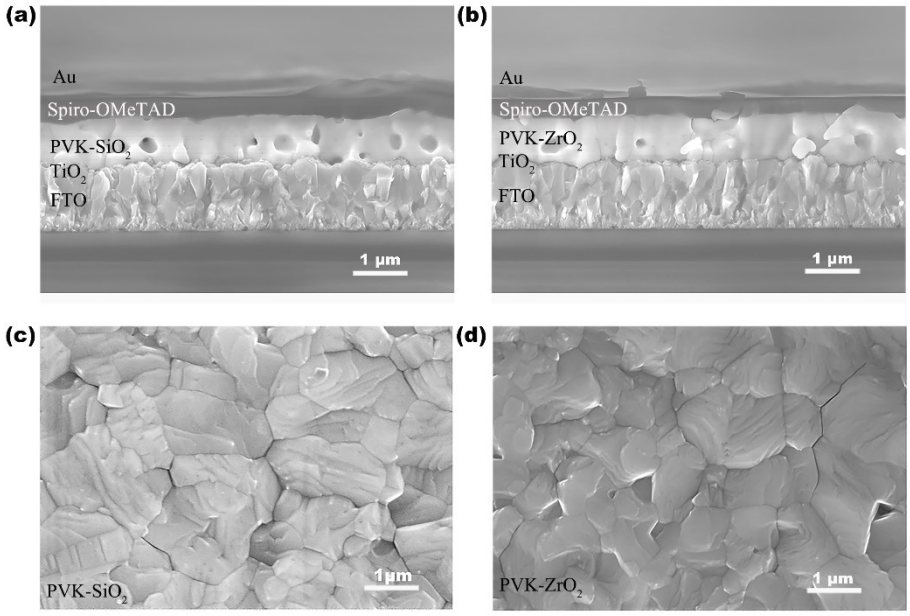

Figure S1. SEM images of the cross-sectional and top views of the SNOPs added into the PVK layer of PSCs: (a-b) The cross-sectional view of PVK-SiO_2 and PVK-ZrO_2; (c-d) The top view of PVK-SiO_2 and PVK-ZrO_2.

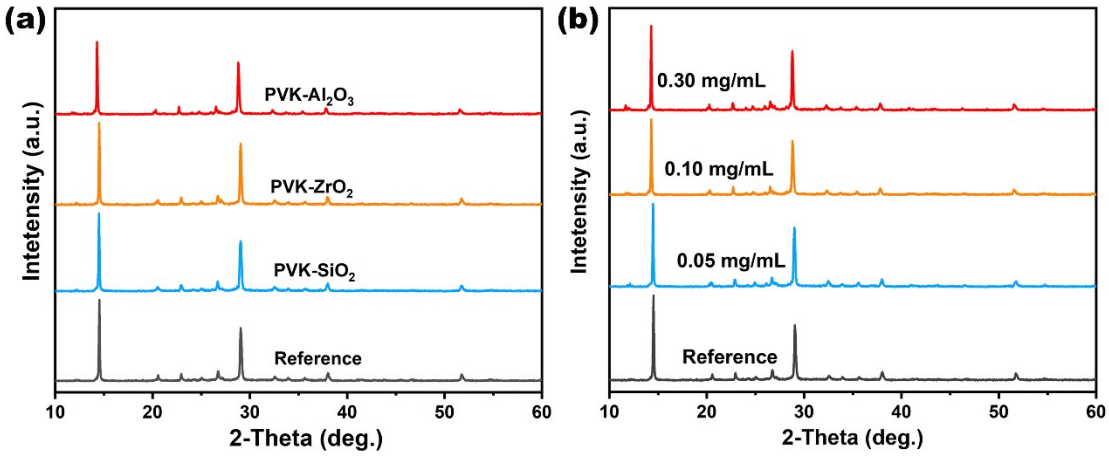

Figure S2. XRD patterns of reference and three SNOPs added into PVK layer: (a) For different SNOPs (SiO_2, ZrO_2, Al_2O_3) and (b) For different concentrations of Al_2O_3.

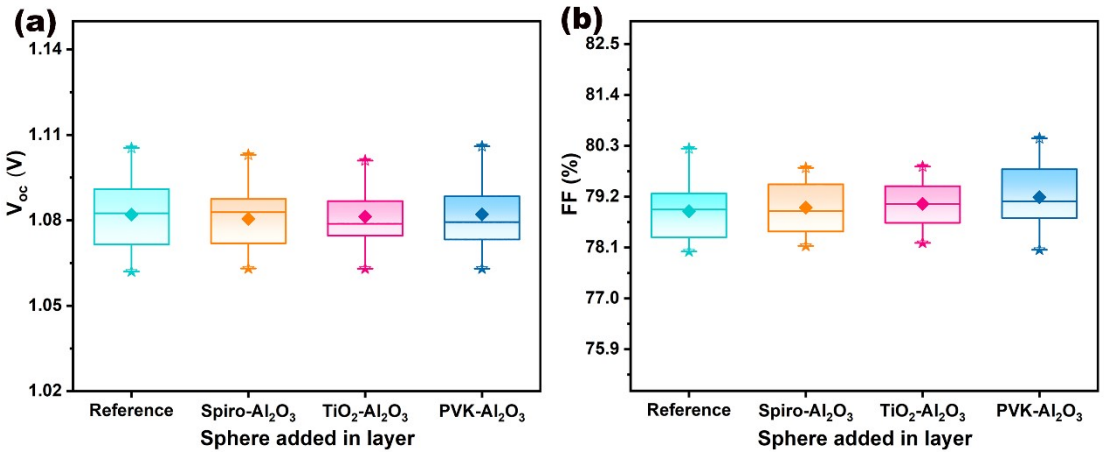

Figure S3. Photovoltaic characterization: Statistical distribution of four key parameters for PSCs (20 devices) in four cases (reference, TiO_2-Al_2O_3, Spiro-Al_2O_3, PVK-Al_2O_3): (a) V_{OC} and (b) FF.

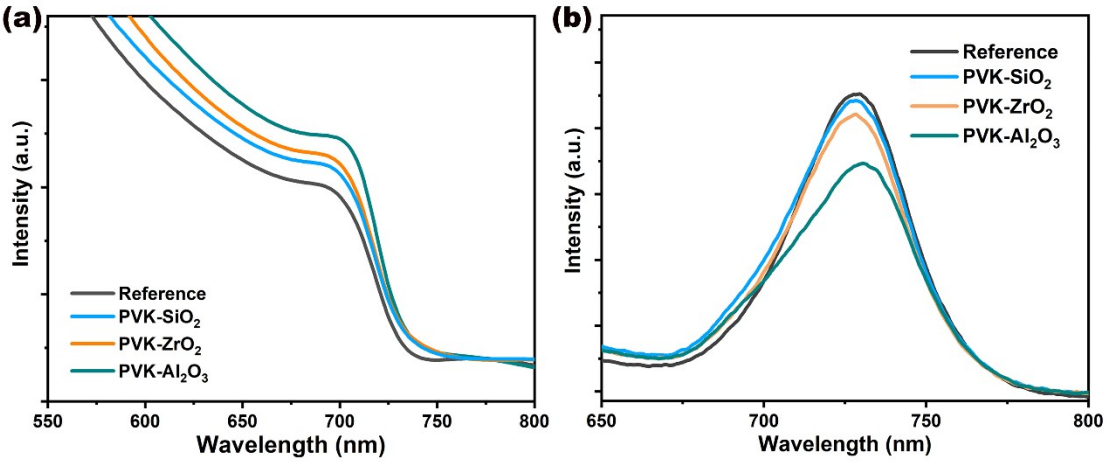

Figure S4. Spectral characterization: (a) Absorption spectra of reference and three SNOPs added into PVK layer of PSCs; (b) PL spectra of reference and three SNOPs added into PVK layer of PSCs.

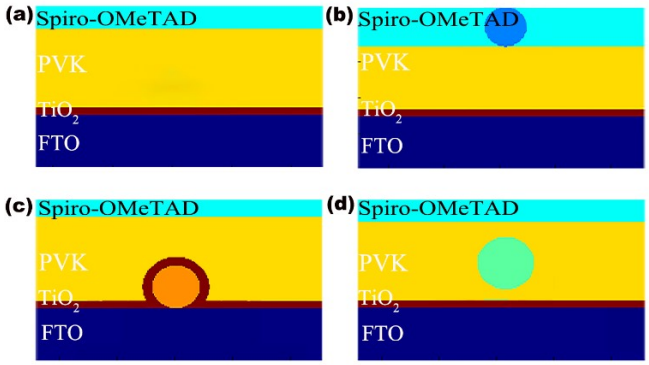

Figure S5. Schematic diagram of simulation of the light intensity distribution of SNOPs added into different layers of PSCs: (a) Reference; (b) Spiro layer; (c) TiO_2 layer; and (d) PVK layer.

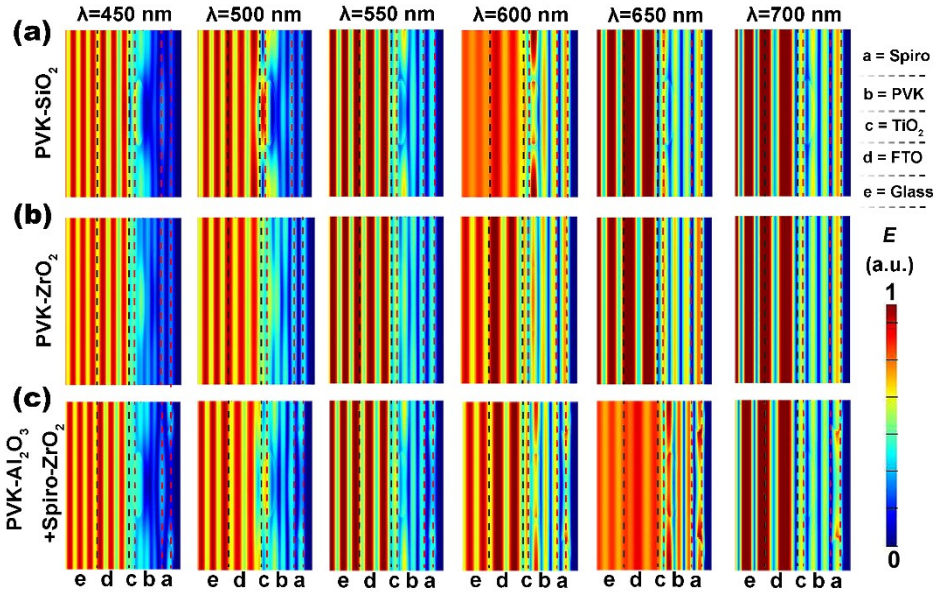

Figure S6. Simulation of the light intensity distribution at six different incident wavelengths in three cases: (a) PVK-SiO_2; (b) PVK-ZrO_2; and (c) PVK-Al_2O_3+PVK-ZrO_2.

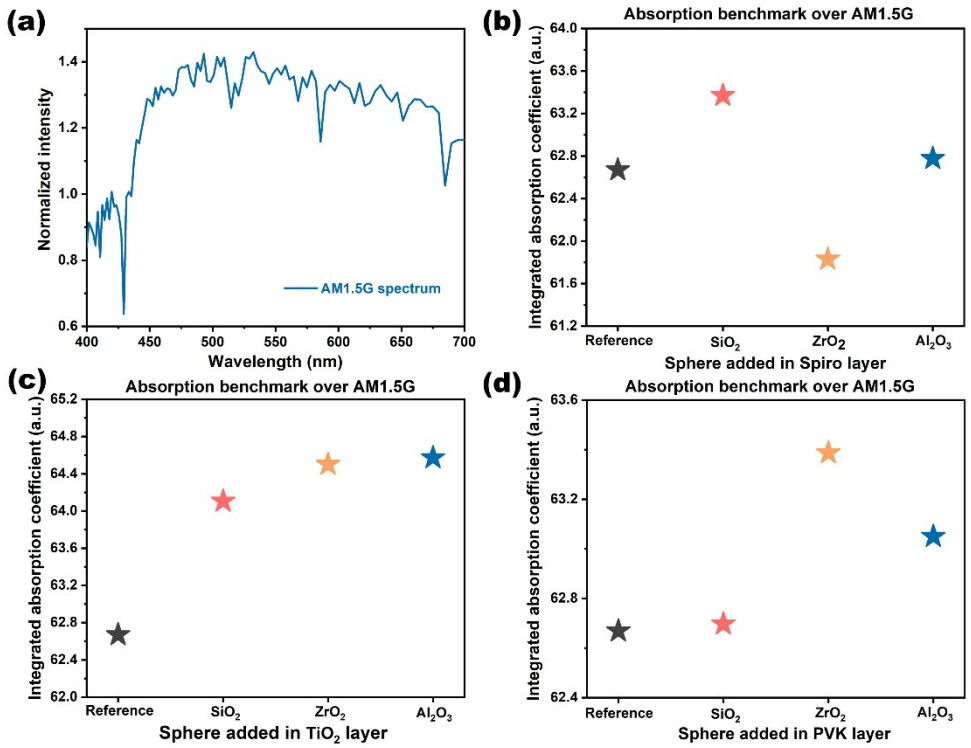

Figure S7. The integrated absorption coefficient of reference and three SNOPs added into different layers of PSCs under absorption benchmark over AM 1.5G (reference, SiO_2, ZrO_2, and Al_2O_3): (a) AM 1.5G spectrum; (b) Spiro layer; (c) TiO_2 layer; and (d) PVK layer.

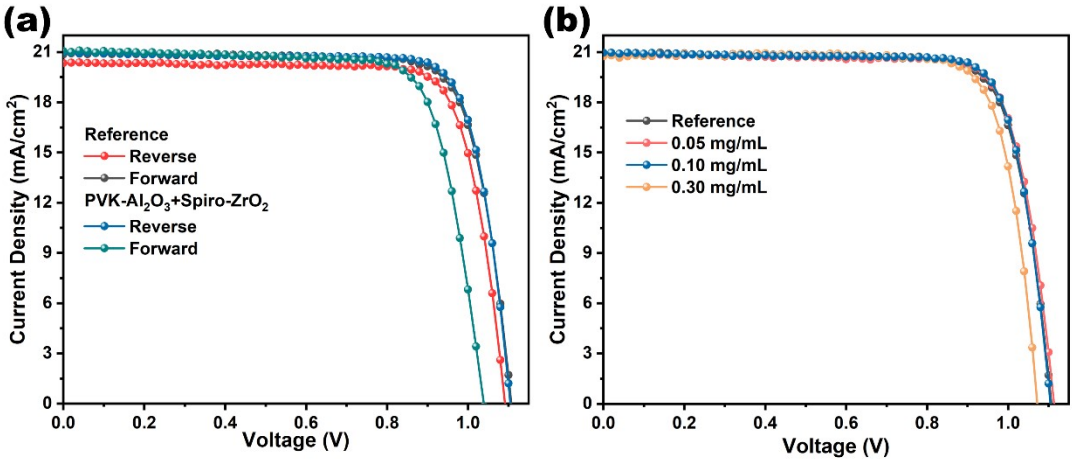

Figure S8. Photovoltaic characterization: (a) *J-V* characteristics of reference and optimized (PVK-Al_2O_3+Spiro-ZrO_2) devices; (b) Based on different concentrations (PVK-Al_2O_3+Spiro-ZrO_2).

Table S1. The photovoltaic parameters of PSCs are extracted from **Figure 2a**.

Device	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
Reference	20.34	1.091	79.71	17.70
Spiro-Al_2O_3	20.57	1.103	79.56	18.05
TiO_2-Al_2O_3	20.66	1.101	79.85	18.16
PVK-Al_2O_3	20.85	1.106	79.29	18.30

Table S2. The photovoltaic parameters of PSCs are extracted from **Figure 2d**.

Device	Scan mode	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
Reference	reverse	20.34	1.091	79.71	17.70
	forward	20.25	1.017	76.75	15.81
PVK-Al_2O_3	reverse	20.85	1.106	79.29	18.30
	forward	20.83	1.100	71.52	16.40

Table S3. The photovoltaic parameters of PSCs are extracted from **Figure 2f**.

Device	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
Reference	20.34	1.091	79.71	17.70
PVK-SiO_2	20.54	1.105	79.71	18.10
PVK-ZrO_2	20.65	1.103	79.57	18.14
PVK-Al_2O_3	20.85	1.106	79.29	18.30

Table S4. The photovoltaic parameters of PSCs are extracted from **Figure S8a**.

Device	Scan mode	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
Reference	reverse	20.85	1.106	79.29	18.30
	forward	20.83	1.100	71.52	16.40
PVK-Al_2O_3 + Spiro-ZrO_2	reverse	20.96	1.103	80.12	18.55
	forward	21.05	1.039	76.52	16.74

Table S5. The photovoltaic parameters of PSCs extracted from **Figure S8b**.

Device	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
Reference	**20.85**	**1.106**	**79.29**	**18.30**
0.05 mg/mL ZrO_2	**20.82**	**1.113**	**79.58**	**18.45**
0.10 mg/mL ZrO_2	**20.96**	**1.103**	**80.12**	**18.55**
0.30 mg/mL ZrO_2	**20.74**	**1.072**	**80.47**	**17.90**