Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Semiconductor plamon-sensitized broadband upconversion and its enhancement on power conversion efficiency of perovskite solar cell

Donglei Zhou, Dali Liu, Junjie Jin, Xu Chen, Wen Xu, Ze Yin, Gencai Pan, Dongyu Li, Hongwei Song**

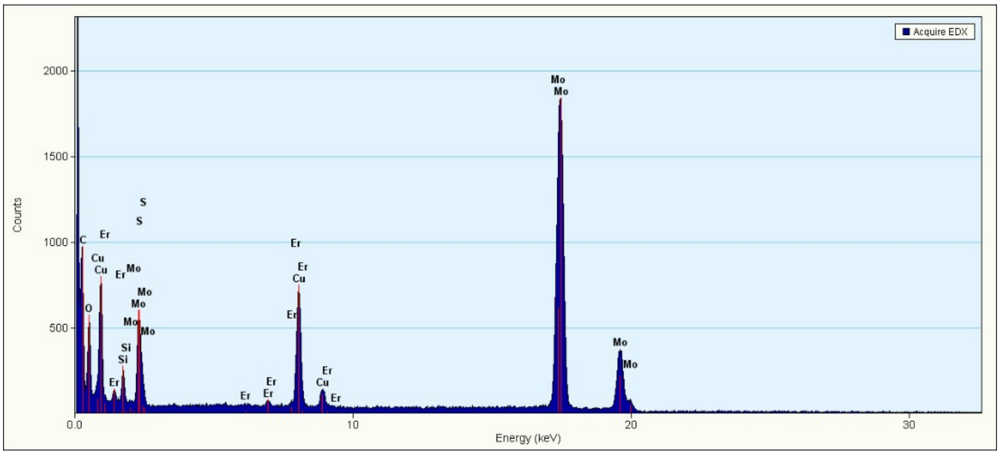

Figure S1 EDX image of $mCu_{2-x}S@SiO_2@Er_2O_3$ nanocomposites.

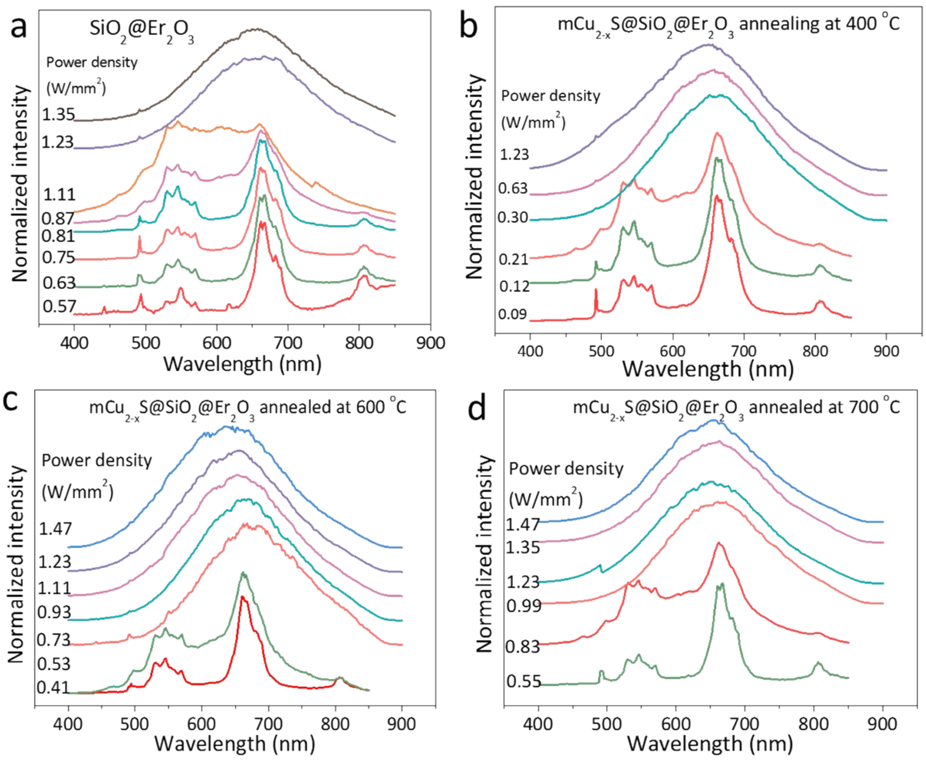

Figure S2 Power-dependent upconversion spectra of $SiO_2@Er_2O_3$ and $mCu_{2-x}S@SiO_2@Er_2O_3$ composites annealed at 400, 600 and 700°C.

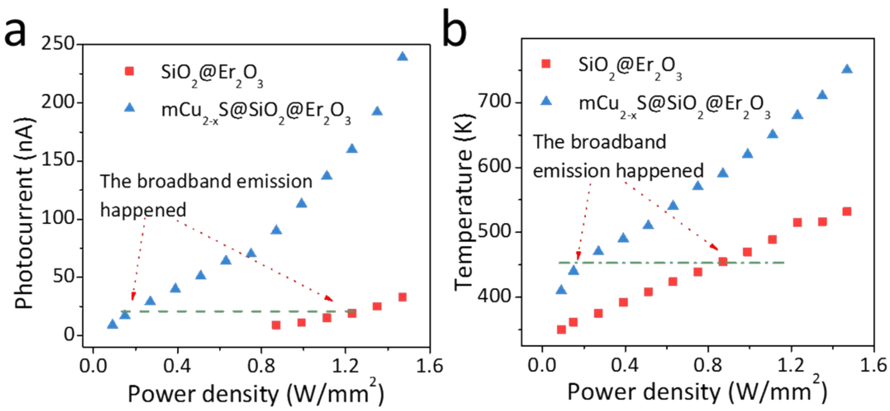

Figure S3 Photocurrent (a) and temperature (b) as a function of excitation power density in the SiO_2 @Er_2O_3 and m$Cu_{2-x}S$@SiO_2 @Er_2O_3 composites samples under 980 nm excitation. The temperature as a function of excitation power was measured by burying a thermocouple thermometer into the powder plate samples in the SiO_2@Er_2O_3 and m$Cu_{2-x}S$@SiO_2@Er_2O_3 composites under 980 nm excitation, respectively. The film for photocurrent test was prepared under 30 MPa pressure to form a dense film.

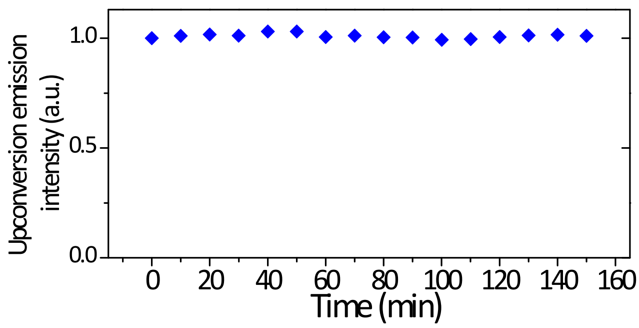

Figure S4 Upconversion emission intensity measured every 10 min under contineous illumination within 160 min of the 980 nm laser (1.23W/mm^2).

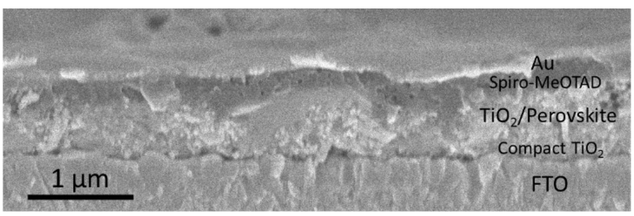

Figure S5 Cross-sectional SEM image of the perovskite solar cell.

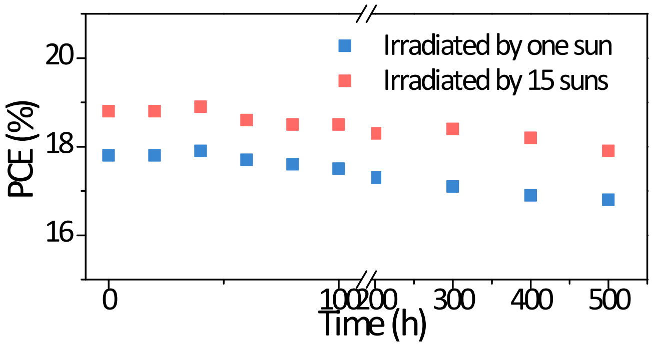

Figure S6 Time-dependent PCE of PSC device with m$Cu_{2-x}S@SiO_2@Er_2O_3$ composites under one sun and 15 suns. The PSC was kept in the glove box (Water content＜1.1ppm, oxygen content＜0.1ppm).

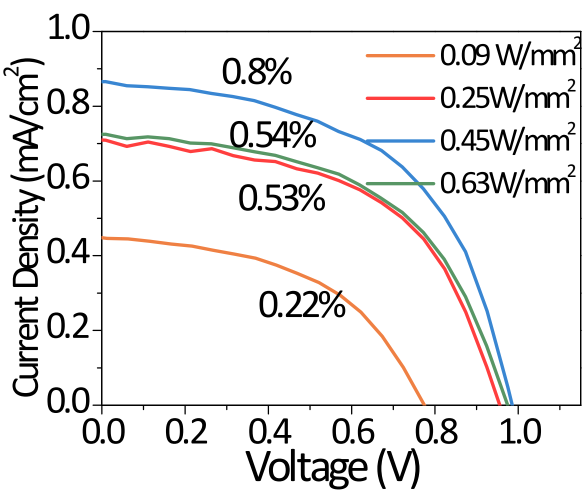

Figure S7 Current-density/voltage curves of solar cell with m$Cu_{2-x}S@SiO_2$ @Er_2O_3 composites under 980 nm laser irradiance.

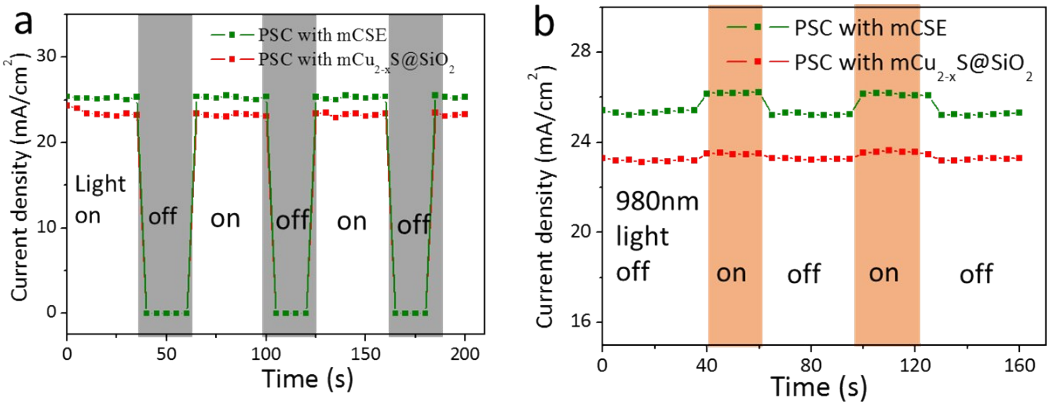

Figure S8 (a) The current transient V.S. time curves with standard sunlight on and off. (b) The current transient V.S. time curves with an additional 980nm light on and off.

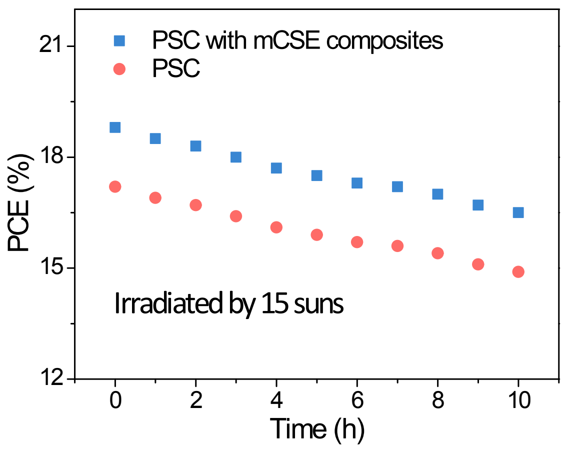

Figure S9 PCEs of PSC with/without $mCu_{2-x}S@SiO_2@Er_2O_3$ composites after irradiated by 15 suns for 10h continuously.

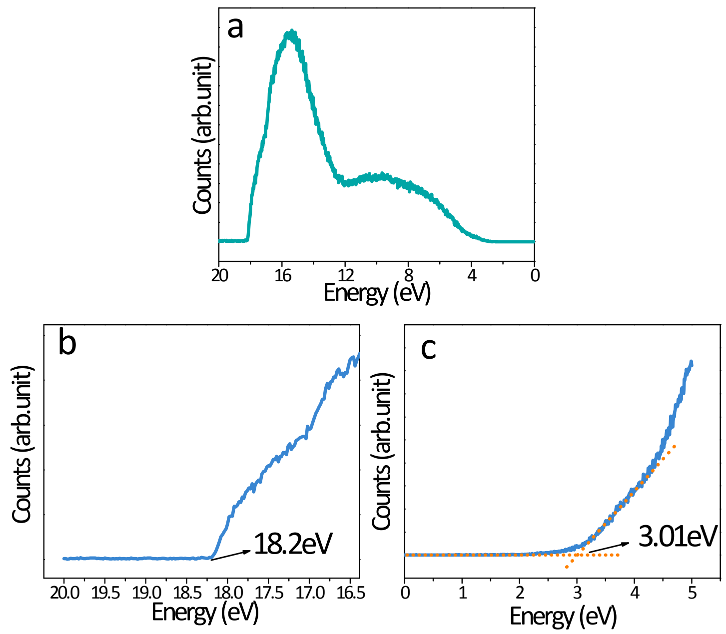

Figure S10 (a) Full UPS valence band spectra of $mCu_{2-x}S@SiO_2@Er_2O_3$ composites. (b) UPS photoemission cutoff and (c) valence band spectra.

The energy level of oxygen defects is 1.9 eV above the valence band. According to UPS spectra, the valence band is 6.01 eV under vacuum level. Therefore, the energy level of oxygen defects is 4.1 eV under vacuum level.

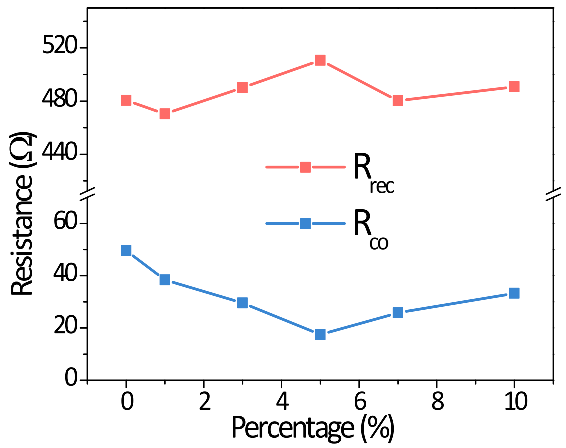

Figure S11 Recombination resistance (R_{rec}) and charge transfer resistance (R_{co}) of pevoskite solar cell with 0-10% percentage of $mCu_{2-x}S@SiO_2@Er_2O_3$ composites.

	Solar Cell	Solar Cell+ $mCu_{2-x}S@SiO_2$	Solar Cell+ $SiO_2@Er_2O_3$	Solar Cell+ $mCu_{2-x}S$ $@SiO_2@Er_2O_3$
Open-circuit voltage (V)	1.07	1.08	1.04	1.1
Short-circuit current (mA)	23.3	23.8	21.2	25.1
Fill factor (%)	65	63	57	64
Efficiency (%)	16.2	16.3	12.6	17.8

Table S1 Open-circuit voltages, short-circuit currents, fill factors and efficiencies of the traditional perovskite solar cell, the cell containing $SiO_2@Er_2O_3$, the cell containing $mCu_{2-x}S@SiO_2$ and the solar cell containing $mCu_{2-x}S@SiO_2@Er_2O_3$ composites.

	Irradiated by one solar constant	Irradiated by 10 solar constant	Irradiated by 15 solar constant
PSC without upconversion composites	21°C	24°C	29°C
PSC with upconversion composites	22°C	25°C	31°C

Table S2 Temperatures of PSCs with/without $mCu_{2-x}S@SiO_2@Er_2O_3$ upconversion composites, which were measured by using a thermocouple. The temperature of ambient air was about 20°C.

	Rco (Ω)	*Rrec (Ω)*
Solar cell	49.62 Ω	480.5Ω
Solar cell+ $@Er_2O_3$	74.34 Ω	445.3 Ω
Solar cell + $mCu_{2-x}S@SiO_2$	53.39 Ω	463.5 Ω
Solar cell + $mCu_{2-x}S@SiO_2$ $@Er_2O_3$ composites	17.43 Ω	510.7 Ω

Table S3 Resistances derived from the Nyquist plots of $CH_3NH_3PbI_3$ perovskite solar cells.

Note 1

The calculation of electric field distribution was calculated using commercial software with a frequency domain solver based on the three-dimensional FDTD method. The FDTD method is an explicit time marching algorithm used to solve Maxwell's curl equations on a discretized spatial grid. The $Cu_{2-x}S$ nanocrystals (diameter: 8 nm) are distributed in the Er_2O_3 shell (thickness: 7 nm) coated SiO_2 sphere (diameter: 40 nm). The refractive index of $Cu_{2-x}S$ nanocrystals was set according to extrapolated n and k curves in the paper[1] by Su-Wen Hsu. The mesh area is 80 nm*80 nm*80 nm. The averaged electric field enhancement factors were obtained by calculating the average value of the electric field intensity enhancement in the mesh range.

Reference:

1. Su-Wen Hsu, Charles Ngo, and Andrea R. Tao*, Tunable and Directional Plasmonic Coupling within Semiconductor Nanodisk Assemblies, Nano Letters, 2014, 14, 2372−2380.