

Electronic Supplementary Information

Three-dimensional titanium oxide nanoarrays for perovskite photovoltaics: surface engineering for cascade charge extraction and beneficial surface passivation†

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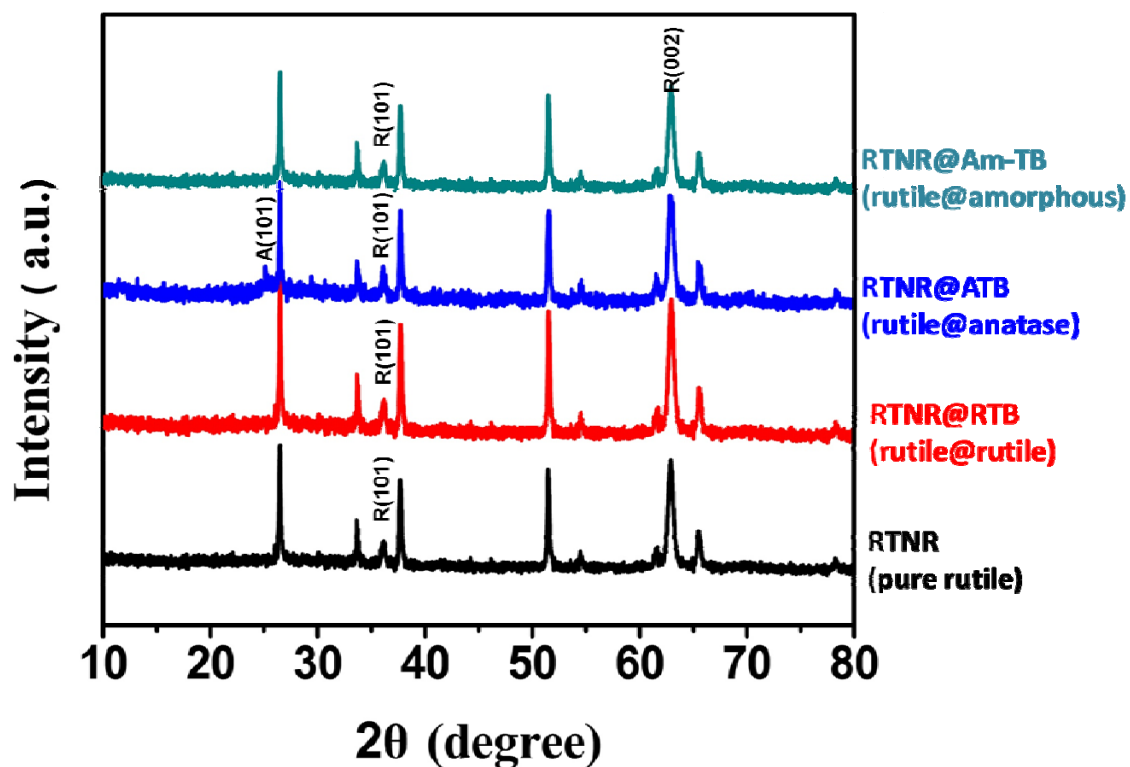


Figure S1. XRD patterns of the TiO₂ nanoarray films grown onto FTO glass showing the pure or mixed crystal phases (A and R indicate anatase and rutile phase).

Table S1. Photovoltaic parameters (J_{sc} , V_{oc} , FF, and PCE) of the PSCs constructed using 1D RTNR array ETLs of different lengths under one sun illumination (AM 1.5 G, 100 mW cm⁻²).

RTNR lengths	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	PCE (%)	Average PCE ^a (%)	FF
120 nm	20.06	840	9.18	8.04±0.56	0.55
600 nm	21.32	884	11.15	9.37±0.68	0.59
850 nm	20.19	816	8.77	7.54±0.47	0.53

^adata for average PCE are calculated from 10 devices.

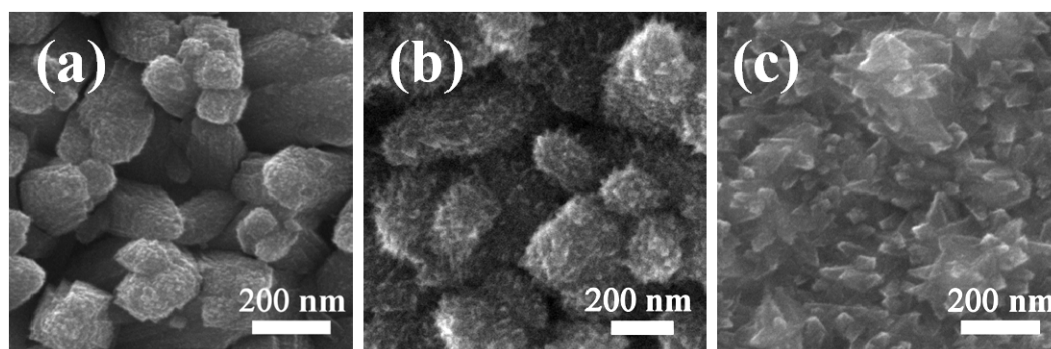


Figure S2. SEM images of the RTNR@RTB films prepared in $\text{TiCl}_3/\text{H}_2\text{O}/\text{HCl}$ at $80\text{ }^\circ\text{C}$ for 2 h with different volumes of TiCl_3 (20 wt% in 2 M HCl): (a) 0.1 mL; (b) 0.2 mL; and (c) 0.3 mL.

Table S2. Photovoltaic parameters (J_{sc} , V_{oc} , FF, and PCE) of the PSCs constructed using RTNR@RTB array ETLs prepared with different TiCl_3 volumes (20 wt% in 2 M HCl) under one sun illumination (AM 1.5 G, 100 mW cm^{-2}).

TiCl_3 volume	J_{sc} (mA cm^{-2})	V_{oc} (mV)	PCE (%)	Average PCE ^a (%)	FF
0.1 mL	21.23	895	11.74	10.22 ± 0.47	0.61
0.2 mL	21.77	914	12.27	10.85 ± 0.47	0.62
0.3 mL	22.19	893	11.60	10.10 ± 0.58	0.59

^adata for average PCE are calculated from 10 devices.

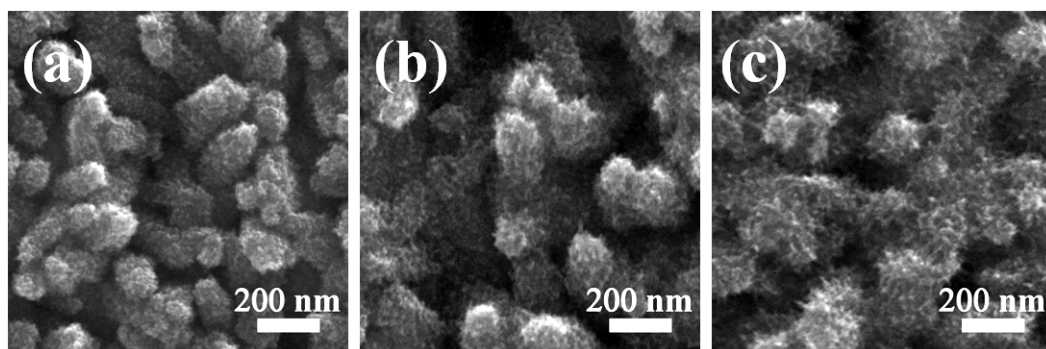


Figure S3. SEM images of the RTNR@ATB films prepared in PTO/H₂O/IPA/DEG at 190 °C for 3 h with different masses of PTO: (a) 6.25 mg; (b) 12.5 mg; and (c) 25.0 mg.

Table S3. Photovoltaic parameters (J_{sc} , V_{oc} , FF, and PCE) of the PSCs constructed using RTNR@ATB array ETLs prepared with different PTO masses under one sun illumination (AM 1.5 G, 100 mW cm⁻²).

PTO mass	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	PCE (%)	Average PCE ^a (%)	FF
6.25 mg	21.47	921	12.38	11.42±0.60	0.63
12.5 mg	21.78	994	14.71	13.12±0.39	0.68
25.0 mg	21.09	957	12.44	11.53±0.45	0.62

^adata for average PCE are calculated from 10 devices.

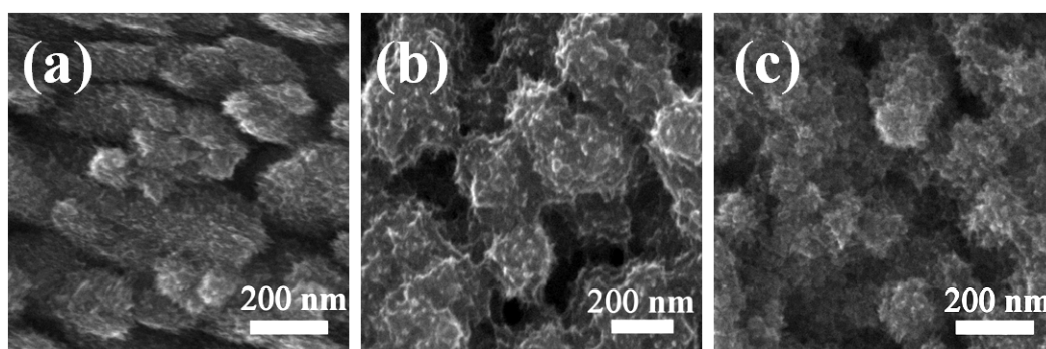


Figure S4. SEM images of the RTNR@Am-TB films prepared in PTO/H₂O at 90 °C for 3 h with different PTO masses: (a) 100 mg; (b) 200 mg; and (c) 300 mg.

Table S4. Photovoltaic parameters (J_{sc} , V_{oc} , FF, and PCE) of the PSCs constructed using RTNR@Am-TB array ETLs prepared with different PTO masses under one sun illumination (AM 1.5 G, 100 mW cm⁻²).

PTO mass	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	PCE (%)	Average PCE ^a (%)	FF
100 mg	19.81	961	13.71	12.43±0.59	0.72
200 mg	21.80	1010	16.06	15.28±0.30	0.73
300 mg	20.51	934	13.94	12.78±0.47	0.73

^adata for average PCE are calculated from 10 devices.

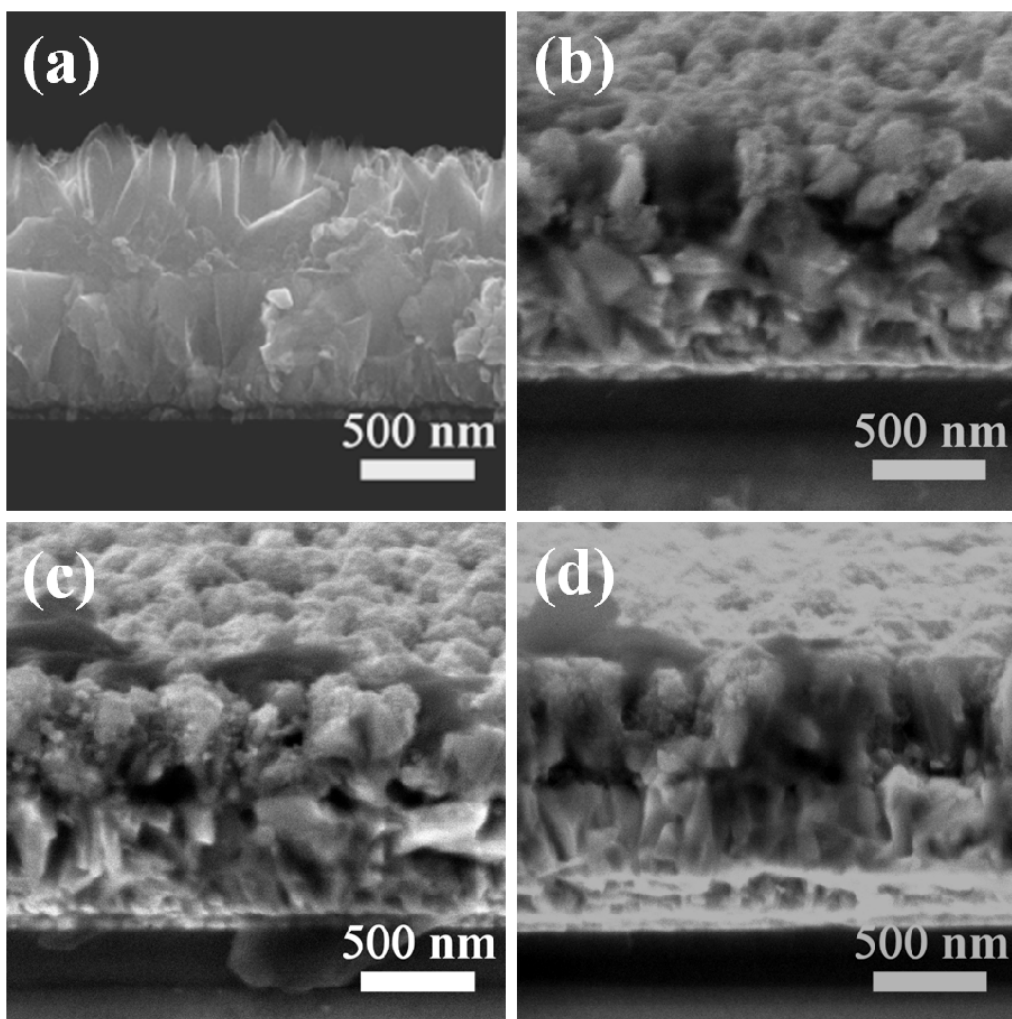


Figure S5. Cross-sectional SEM images of different TiO₂ nanoarrays: (a) RTNR; (b) RTNR@RTB; (c) RTNR@ATB and (d) RTNR@Am-TB.

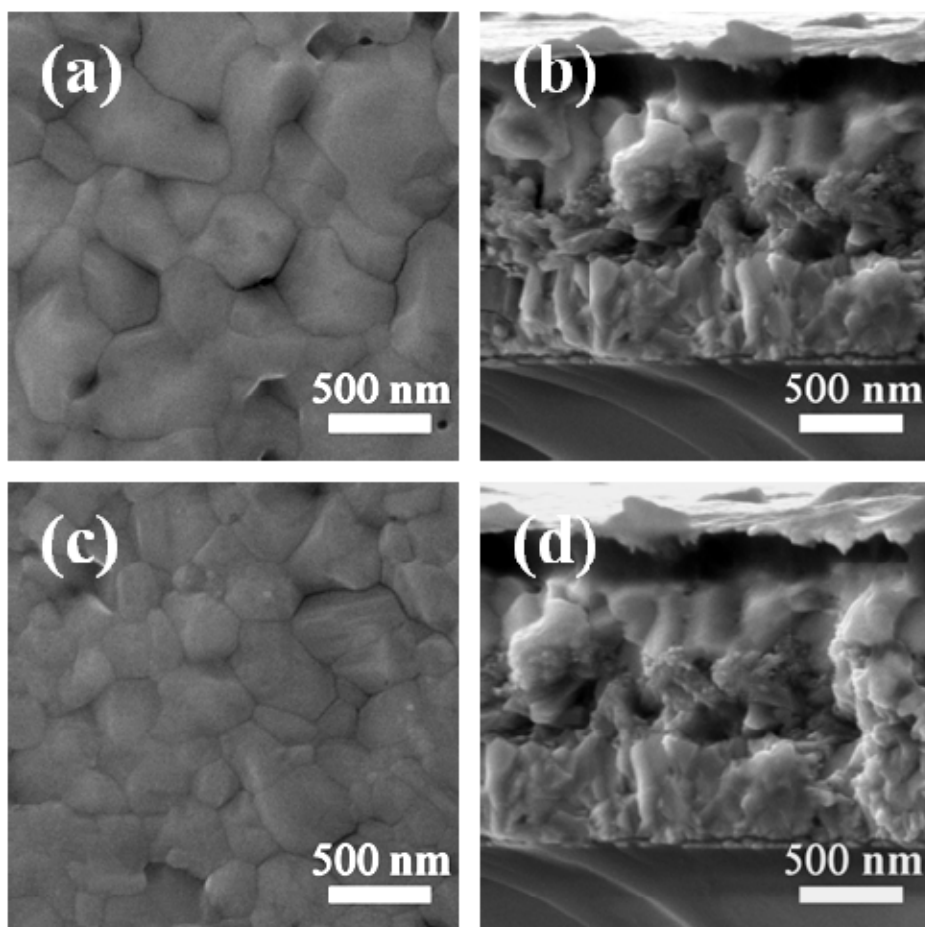


Figure S6. Top-view SEM images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ capping layer grown on (a) FTO/RTNR@RTB and (c) FTO/RTNR@ATB electrodes. Cross-sectional SEM images of complete PSC devices: (b) FTO/RTNR@RTB/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /spiro-OMeTAD/Au and (d) FTO/RTNR@ATB/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /spiro-OMeTAD/Au.

Table S5 Morphological parameters of the perovskite in the FTO/ TiO_2 nanoarrays/Perovskite electrodes used in this study. D is the grain size distribution of the perovskite crystal. L is the perovskite capping layer thickness.

TiO_2 nanoarrays	D (nm)	L (nm)
RTNR	350-950	450 ± 10
RTNR@RTB	320-900	350 ± 10
RTNR@ATB	250-550	300 ± 10
RTNR@Am-TB	100-500	300 ± 10

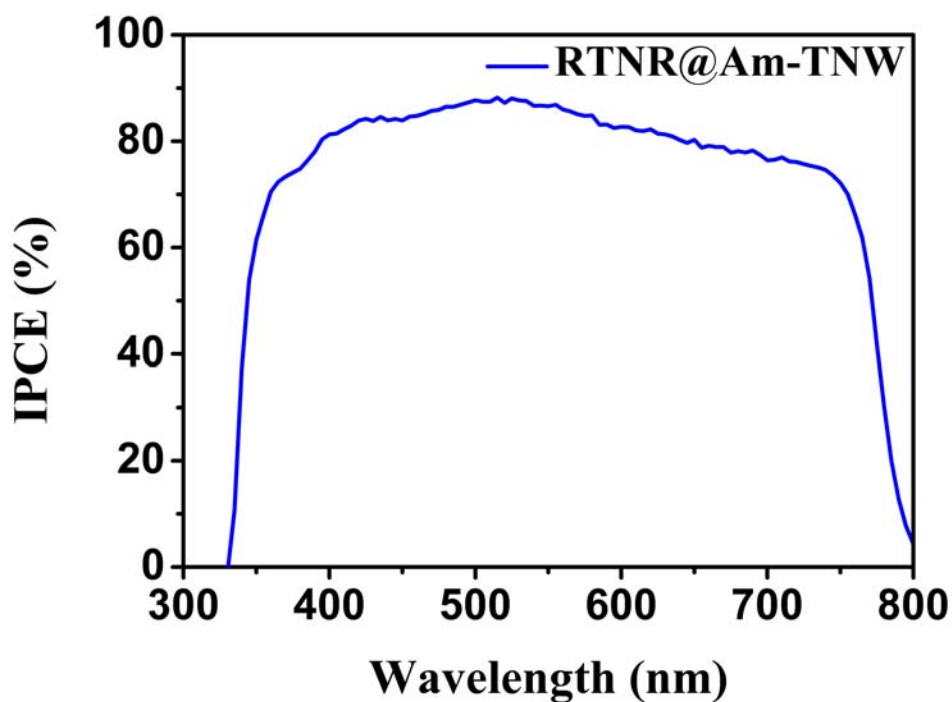


Figure S7. IPCE spectrum of a PSC based on 3D RTNR@Am-TB nanoarray ETL.

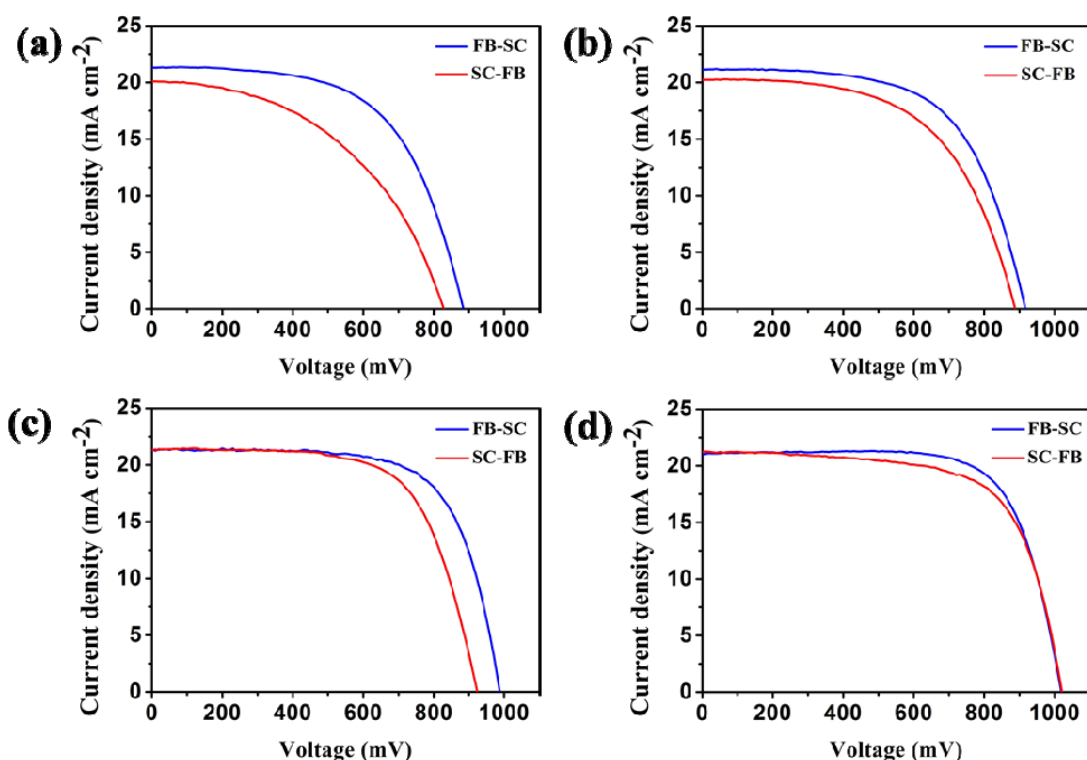


Figure S8. FB-SC (reverse scan: from forward bias to short-circuit) and SC-FB (forward scan: from short-circuit to forward bias) J - V curves measured under AM 1.5 simulated solar light with a scan rate of 0.1 V s^{-1} for devices prepared using: (a) RTNR; (b) RTNR@RTB; (c) RTNR@ATB and (d) RTNR@Am-TB ETLs.

Table S6. Photovoltaic parameters of the PSCs fabricated using different TiO₂ nanoarrays in reverse (FB-SC) and forward (SC-FB) scanning directions under one sun illumination (AM 1.5G, 100 mW cm⁻²).

PSC	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	PCE (%)	FF
RTNR-FB-SC	21.32	884	11.15	0.59
RTNR-SC-FB	20.09	829	7.81	0.47
RTNR@RTB-FB-SC	21.77	914	12.27	0.62
RTNR@RTB-SC-FB	20.23	888	10.24	0.57
RTNR@ATB-FB-SC	21.78	994	14.71	0.68
RTNR@ATB-SC-FB	20.32	924	13.05	0.66
RTNR@Am-TB-FB-SC	21.80	1010	16.06	0.73
RTNR@Am-TB-SC-FB	21.50	1006	14.62	0.68

Data displayed above were based on the champion cell for each experimental condition. At least 3 devices were tested for each condition to confirm the hysteresis behavior.

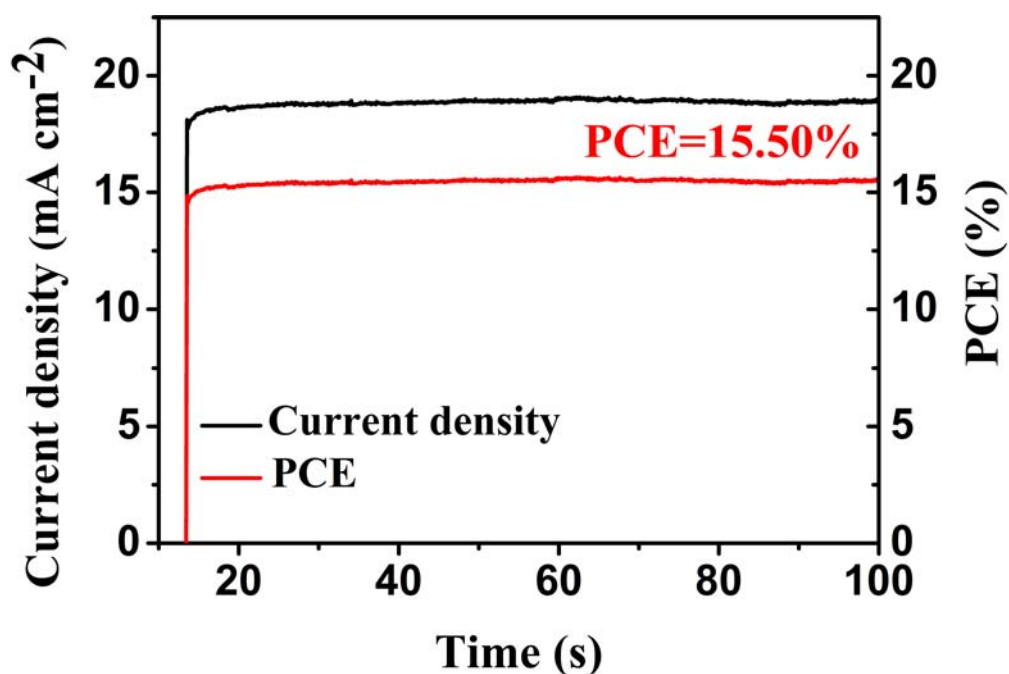


Figure S9. Steady-state current and stabilized power conversion efficiency for the best-performing cell based on RTNR@Am-TB measured at a maximum power point (0.82 V).