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Figue S1. Fourier transform infrared transmission spectra of the films. Fourier transform infrared transmission spectra of PVA and *c*PVA films with different ratios of crosslinker (boric acid, 1%, 3%, 5%, 10% and 20%). The wavenumber bands centered at 661 cm<sup>-1</sup> and 3300 cm<sup>-1</sup> correspond B-O group and -OH group respectively.



Figure S2. The transmission of the electrodes after annealed at 200 °C for different times. The transmission of the AgNWs-em-PVA (a) and AgNWs-em-cPVA (b) electrodes after annealed at 200 °C for 0 min, 5 min, 10 min and 20 min. (c) The transmission at 550 nm of AgNWs-em-PVA and AgNWs-em-cPVA electrodes after annealed at 200 °C for different durations. Data are presented as mean values  $\pm$  standard deviation over 10 samples for each electrode. Curves drawn on top of data are guides to the eye.



**Figure S3. The changes in color and transmittance of the electrodes after annealed at 160 °C for different times.** Photos of color changes (a) and transmittance (b) of the AgNWs-em-PVA (87%) electrodes after annealed at 160 °C for 0 min, 5 min, 10 min and 20 min. Curves drawn on top of data are guides to the eye.



AgNWs-em-PVA (87%)

AgNWs-em-PVA

AgNWs-em-cPVA

Figure S4. The photos of the electrodes used for testing moisture adsorption rate. The electrode of the AgNWs-em-PVA (87%), AgNWs-em-PVA and AgNWs-em-*c*PVA electrodes, with dimensions of 9.5 cm  $\times$  9.5 cm, were adhered to glass/PDMS substrates and exposed in an environment with a humidity of 60% and a temperature of 25 °C.



Figure S5. The moisture adsorption rate of the electrodes. The rate of change in the AgNWsem-PVA (87%) electrode mass (calculated as the difference between real-time mass and initial mass, divided by the initial mass) varies with the duration of placement. Data are presented as mean values  $\pm$  standard deviation over 10 samples. Curves drawn on top of data are guides to the eye.



**Figure S6. Fourier transform infrared transmission spectrum of the** *c***PVA.** Fourier transform infrared transmission spectrum of *c*PVA films with crosslinking degree of 5% (b) and 20% (b). The inset in (b) shows photographs of a 20% crosslinked PVA film before and after annealing at 200 °C for 60 minutes. Curves drawn on top of data are guides to the eye.



Figure S7. Thermal stability of 1-cm<sup>2</sup> flexible devices based on AgNWs-em-*c*PVA electrodes at 80 °C in a N<sub>2</sub>-filled glovebox. Data are presented as mean values  $\pm$  standard deviation over 10 samples. Curves drawn on top of data are guides to the eye.



**Figure S8.** The transmittance of the UV filter with the wavelength from 300 nm to 1,000 nm. Curves drawn on top of data are guides to the eye.

Substrate	Placement time	$V_{\rm OC}({ m V})$	$J_{ m SC}$ (mA/cm <sup>2</sup> )	FF	PCE (%)
AgNWs-em-PVA	0 h	0.84	25.27	0.76	$\frac{16.27}{(16.11\pm0.14)^{a}}$
	24 h	0.84	25.19	0.73	15.27 $(15.18 \pm 0.25)^{a}$
	96 h	0.83	25.13	0.68	14.24 $(14.08 \pm 0.38)^{a}$
	168 h	0.83	25.09	0.65	13.47 $(13.41 \pm 0.49)^{a}$
	0 h	0.84	25.32	0.77	16.38 (16.27 ± 0.13) <sup>a</sup>
	24 h	0.84	25.29	0.76	16.14 (16.07 ± 0.15) <sup>a</sup>
ади ws-сш-сг V А	96 h	0.84	25.27	0.76	16.11 (16.04 ± 0.18) <sup>a</sup>
	168 h	0.84	25.31	0.75	15.92 (15.89 ± 0.19) <sup>a</sup>

**Table S1.** Photovoltaic parameters of flexible OSCs (active area:  $1 \text{ cm}^2$ ) based on the AgNWs-em-PVA and AgNWs-em-*c*PVA electrodes after being exposed in air with a R.H. of 60% and temperature of 25 °C for different time. The configuration of flexible OSCs is AgNWs-em-PVA or AgNWs-em-*c*PVA/PEI-Zn/PM6:BTP-eC9:PC<sub>71</sub>BM/MoO<sub>3</sub>/Ag.

<sup>*a*</sup>Data are presented as mean values  $\pm$  standard deviation from 15 devices.

**Table S2.** Photovoltaic parameters of flexible OSCs (active area:  $1 \text{ cm}^2$ ) based on the AgNWs-em-PVA or AgNWs-em-*c*PVA electrodes with the annealing temperature of the electron transport layer at 200 °C. The configuration of flexible OSCs is AgNWs-em-PVA/PEI-Zn/PM6:BTP-eC9:PC<sub>71</sub>BM/MoO<sub>3</sub>/Ag.

Substrate	$V_{\rm OC}({ m V})$	$J_{ m SC}$ (mA/cm <sup>2</sup> )	FF	PCE (%)
AgNWs-em-PVA	0.84	23.14	0.72	$14.07~(13.97\pm0.11)^{\rm a}$
AgNWs-em-cPVA	0.84	25.26	0.76	16.13 (16.08 ± 0.12) <sup>a</sup>

<sup>*a*</sup>Data are presented as mean values  $\pm$  standard deviation from 15 devices.

Year	Device structure	Area / cm <sup>2</sup>	PCE / %
2011	PET/Cr/Al/Cr/P3HT:PCBM/PEDOT:PSS/Au-grid	13.2	2.2 <sup>1</sup>
2012	PET/Ag/ZnO/P3HT:PCBM/PEDOT:PSS/Ag	35.5	0.44 <sup>2</sup>
2014	Ag grid&HC PEDOT:PSS/ZnO/MH301:PCBM/PFN/PEDOT:PSS(HTL)/ZnO/M H306:PCBM/PFN/PEDOT:PSS(HTL)/HC PEDOT:PSS&Ag grid	52.2	1.76 <sup>3</sup>
2015	DET/Cr/A1/Cr/D2UT.DCDM/DEDOT.DSS/Accrid	32.55	1.78 4
	PET/CI/AI/CI/PSHT:PCBM/PEDOT:PSS/Ag Ond	6.10	2.72 4
2019	Embedded silver grid substrate/PEDOT:PSS/ZnO/P3HT:PCBM/PEDOT:PSS/Ag	36	1.84 5
2020	PET/Ag-grid/PEDOT:PSS/ZnO/PTB7-	25	10.09 6
	Th:COi8DFIC:PCBM/MoO <sub>3</sub> /Ag	50	9.05 <sup>6</sup>
2022	PET/Ag-grid/PEDOT:PSS/ZnO/PM6:Qx-1/MoO <sub>3</sub> /Ag	30	12.2 7
2023	PET/Ag-grid/PEDOT:PSS/ZnO/AL/MoO <sub>3</sub> /Ag	30	13.08 8
2023	PET/Ag/PEI-Zn/PM6:BTP-eC9/PEDOT:F/AgNWs-polymer	21	12.3 <sup>9</sup>
2023	PET/Ag-grid/PEDOT:PSS/ZnO/AL/MoO <sub>3</sub> /Ag	46.2	13.25 10
2024	AgNWs-em-PVA/PEI-Zn/PM6:BTP-eC9:PC <sub>71</sub> BM/MoO <sub>3</sub> /Ag	41	14.04 11
this work	AgNWs-em-cPVA/PEI-Zn/PM6:BTP-eC9:PC <sub>71</sub> BM/MoO <sub>3</sub> /Ag	52.3	14.78

**Table S3.** Summary of the efficiency of flexible large-area modules prepared based on non-ITO electrodes.

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