

## Supporting Information

### **Hybrid 3D Nanostructures Based Hole Transport Layer for Highly Efficient Inverted Perovskite Solar Cells**

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Table S1. The average diameter and thickness of Cr:CuGaO<sub>2</sub>-CC nanocrystals with different Cr doping concentrations.

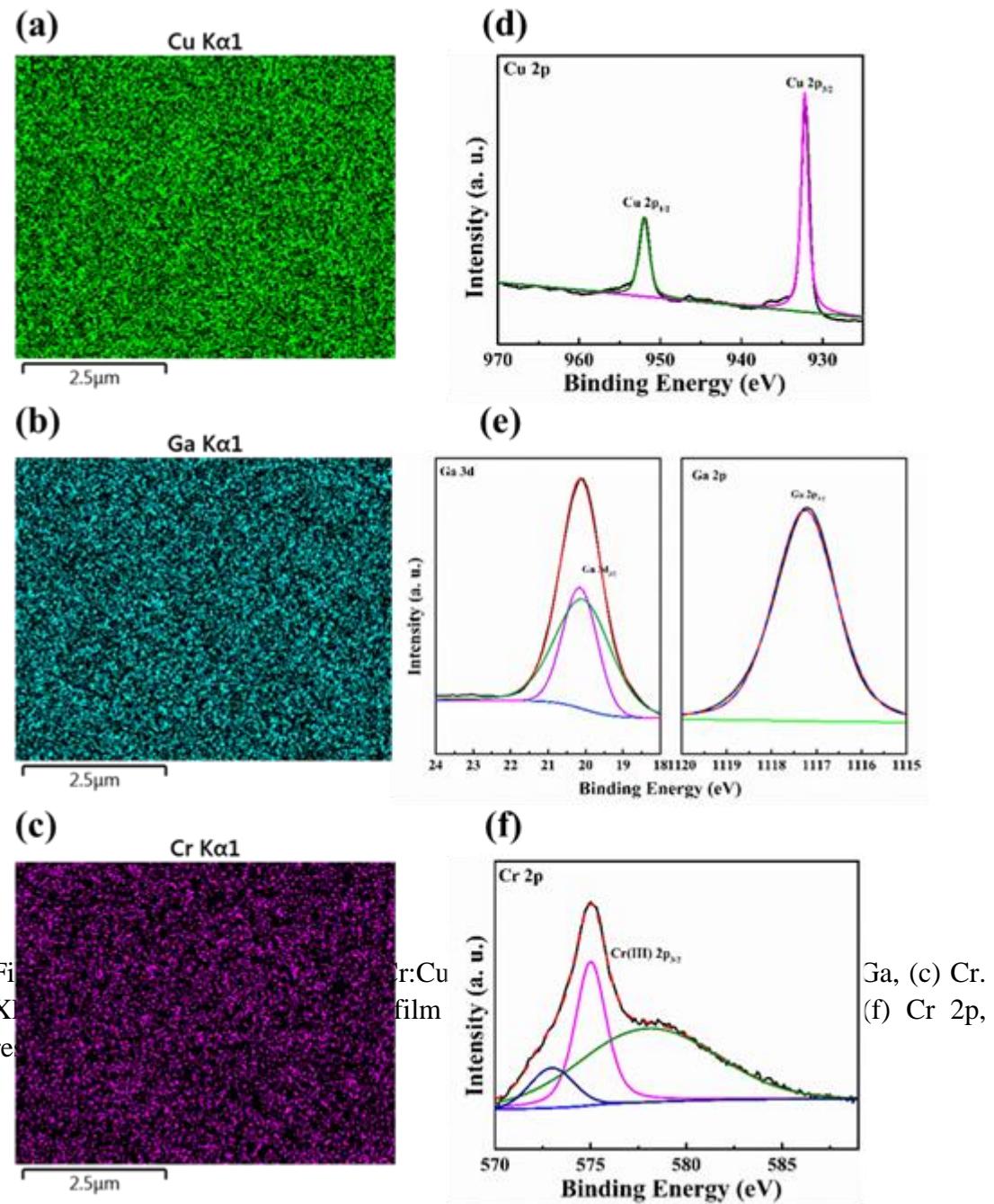
Cr doping content	Average diameter (nm)	Thickness (nm)
1%	63±5.00	8±2.05
5%	39±4.56	8±1.94
7%	32±3.95	10±4.39

Table S2. The champion photovoltaic performance based on NiO<sub>x</sub> and Cr:CuGaO<sub>2</sub>-CC/NiO<sub>x</sub> based PSCs.

HTL	Scan direction	J <sub>SC</sub> (mA/cm <sup>-2</sup> )	V <sub>O</sub> C (V)	FF	Best PCE (%)	Average PCE(%)
Cr:CuGaO <sub>2</sub> -CC/NiO <sub>x</sub>	Forward	22.93	1.08	0.80	19.91	18.26±0.78
	Reverse	22.67	1.08	0.80	19.49	
Cr:CuGaO <sub>2</sub> -CC	Forward	21.06	1.02	0.70	14.96	12.00±0.91
	Reverse	19.60	1.01	0.68	13.46	
NiO <sub>x</sub>	Forward	22.02	1.08	0.75	17.91	16.73±0.60
	Reverse	21.45	1.07	0.73	16.75	

Table S3. Performance of the reported planar inverted PSCs based on 2D HTLs.

Device Architecture		$V_{oc}$ (V)	$J_{sc}$ (mA cm $^{-2}$ )	FF	PCE (%)	Method	Ref.
ITO/PEDOT:PSS+GO/MAPbI <sub>3</sub> /PC BM/ZnO/Ag		1.02	21.55	0.82	18.09	wet chemical	<sup>1</sup>
ITO/PEDOT:PSS+GO+Glucose/MAPbI <sub>3</sub> /PCB M/Ag		1.05	20.50	0.70	12.80	wet chemical	<sup>2</sup>
ITO/PEDOT:PSS+AgOTf GO/MAPbI <sub>3</sub> /PCBM/Ag	doped	0.88	19.18	0.71	11.90	CVD	<sup>3</sup>
ITO/MoO <sub>x</sub> +GO/MAPbI <sub>3</sub> /PCBM/Ag		0.99	21.80	0.77	16.70	wet chemical	<sup>4</sup>
ITO/NGGO/MAPbI <sub>3</sub> /ZnO/Al		1.00	17.93	0.72	12.94	wet chemical	<sup>5</sup>
ITO/PEDOT:PSS/GO:NH <sub>3</sub> /MAPbI <sub>3</sub> /PCBM/A g		1.03	22.06	0.71	16.11	wet chemical	<sup>6</sup>
ITO/PEDOT:PSS/oxo-G1/MAPbI <sub>3</sub> /ZnO/Al		1.08	18.06	0.78	15.20	wet chemical	<sup>7</sup>
ITO/r-Go/PTAA/MAPbI <sub>3</sub> /PCBM/BCP/Ag		1.09	20.30	0.78	17.20	wet chemical	<sup>8</sup>
ITO/MoS <sub>2</sub> /MAPbI <sub>3</sub> /PCBM/Li/Ag		0.96	14.89	0.67	9.53	Liquid exfoliated	<sup>9</sup>
ITO/MoS <sub>2</sub> /MAPbI <sub>3</sub> /PCBM/Ag		0.84	12.60	0.57	6.01	UV/O	<sup>10</sup>
ITO/MoS <sub>2</sub> /MAPbI <sub>3</sub> /PCBM/BCP/Ag		0.88	20.94	0.78	14.35	Liquid exfoliated	<sup>11</sup>
ITO/WS <sub>2</sub> /MAPbI <sub>3</sub> /C <sub>60</sub> /BCP/Ag		0.97	21.22	0.73	15.00	Liquid exfoliated	<sup>11</sup>
ITO/PEDOT:PSS/BPQDs/MAPbI <sub>3</sub> /PCBM/Ag		1.01	20.13	0.80	16.69	Liquid exfoliated	<sup>12</sup>
ITO/PTAA/MoS <sub>2</sub> /MAPbI <sub>3</sub> /PCBM/PFN/Ag		1.01	20.71	0.78	16.42	Liquid exfoliated	<sup>13</sup>
ITO/MoS <sub>2</sub> /MAPbI <sub>3</sub> /TiO <sub>2</sub> /Ag		0.93	26.25	0.84	20.43	Liquid exfoliated	<sup>14</sup>
<b>ITO/Cr:CuGaO<sub>2</sub>-cc/NiO<sub>x</sub>/MAPbI<sub>3-x</sub>Cl<sub>x</sub>/PC BM:C<sub>60</sub>/Zracac/Ag</b>	<b>1.08</b>	<b>22.93</b>	<b>0.81</b>	<b>19.91</b>	<b>NPs in solution</b>	<b>this work</b>	



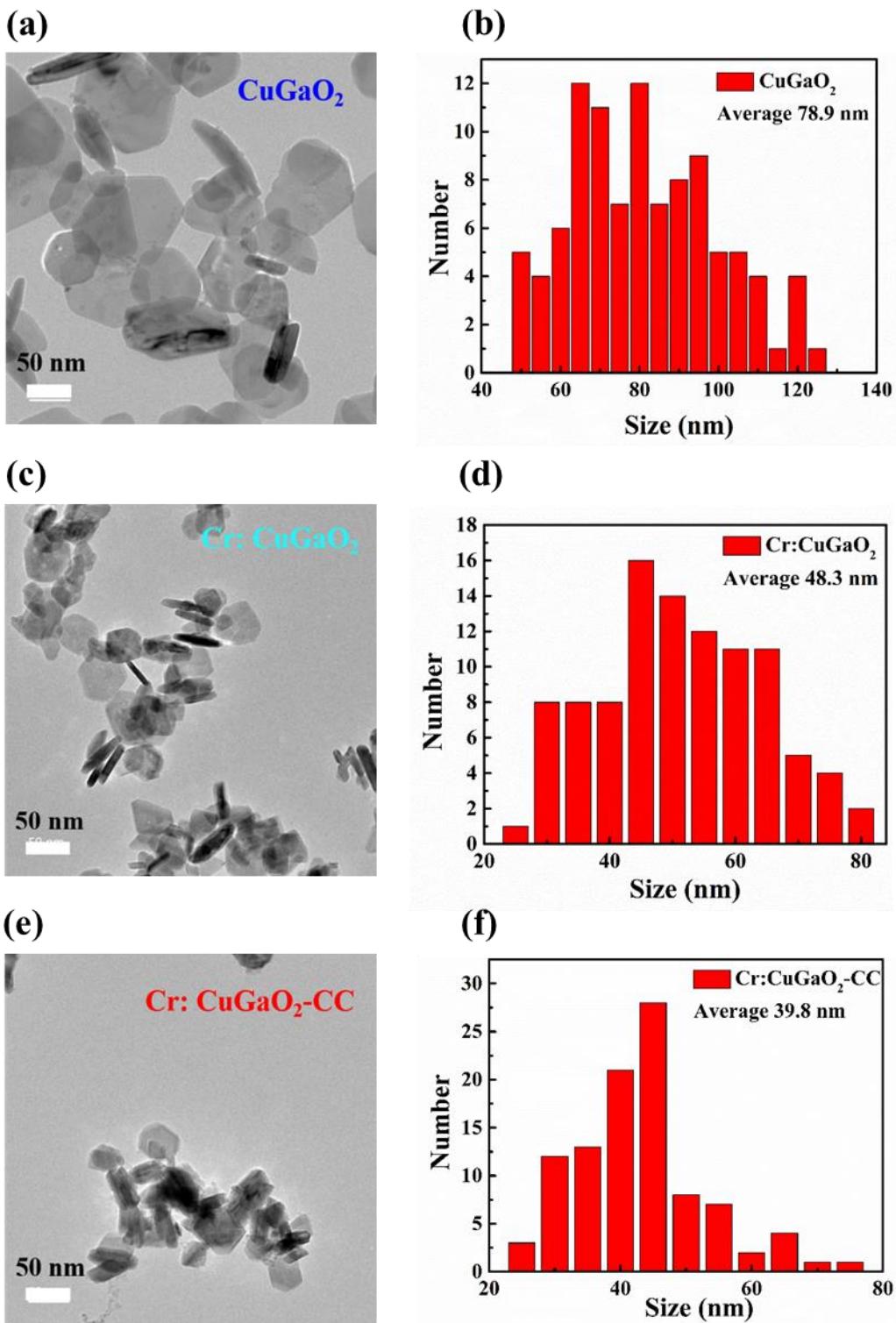


Figure S2. TEM images of (a)  $\text{CuGaO}_2$ , (c)  $\text{Cr:CuGaO}_2$ , and (e)  $\text{Cr:CuGaO}_2\text{-CC}$  nanocrystals. The size distribution of (b)  $\text{CuGaO}_2$ , (d)  $\text{Cr:CuGaO}_2$ , and (f)  $\text{Cr:CuGaO}_2\text{-CC}$  nanocrystals.

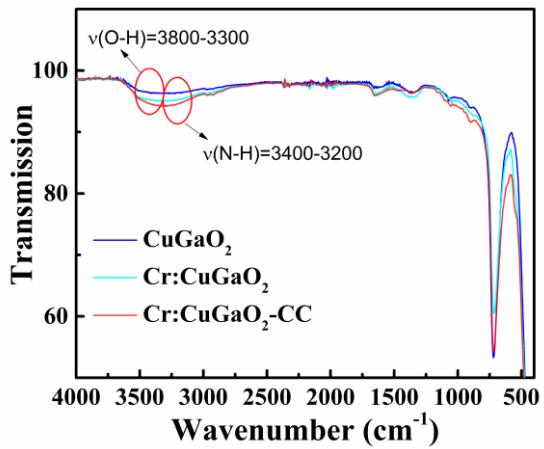


Figure S3. FTIR spectra of as-synthesized of CuGaO<sub>2</sub>, Cr:CuGaO<sub>2</sub>, and Cr:CuGaO<sub>2</sub>-CC nanocrystals.

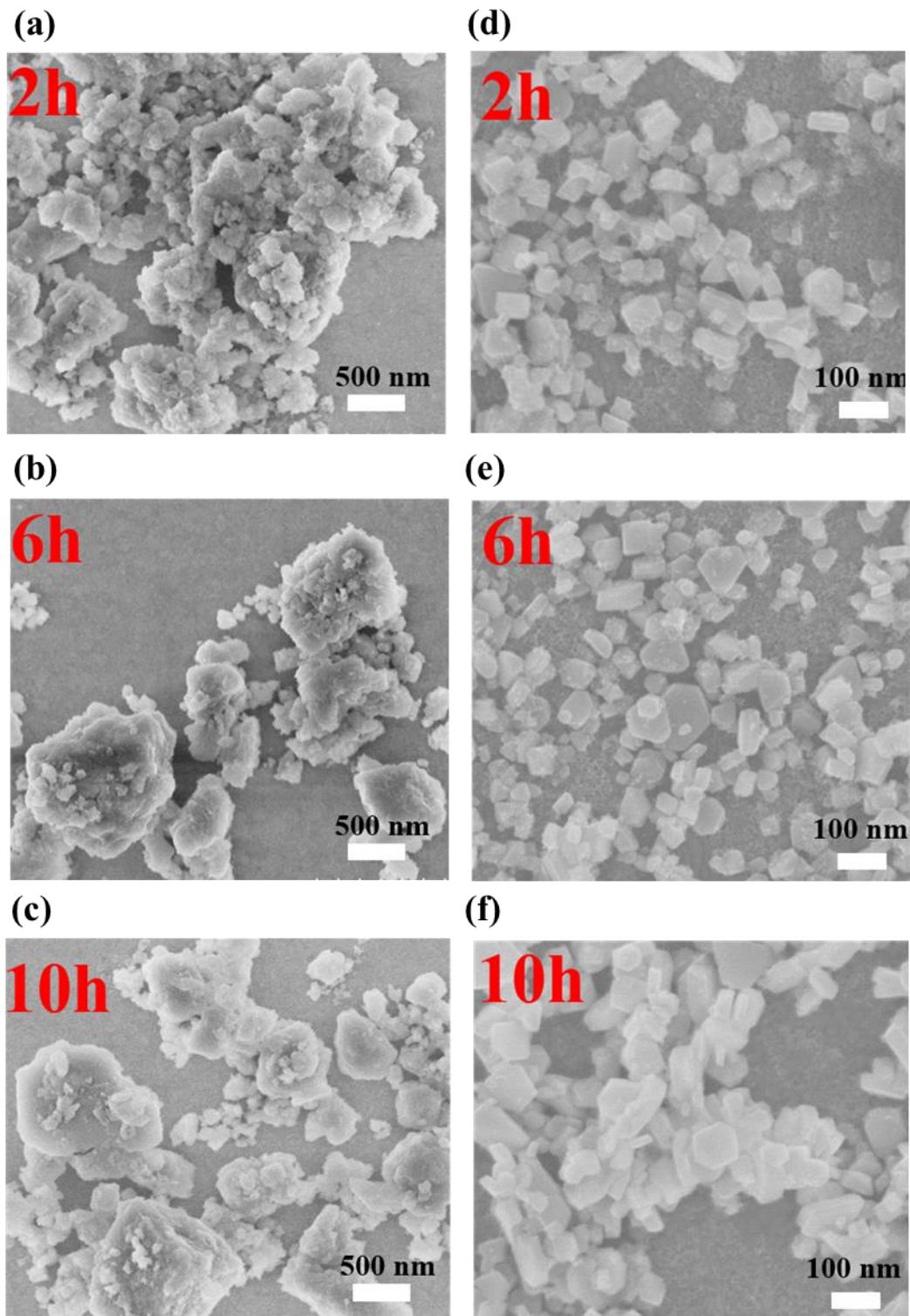


Figure S4. SEM images of the precursor before hydrothermal treatment under (a) 2h, (b) 6h, and (c) 10h aging time and the final Cr:CuGaO<sub>2</sub>-CC nanocrystals under (d) 2h, (e) 6h, and (f) 10h aging.

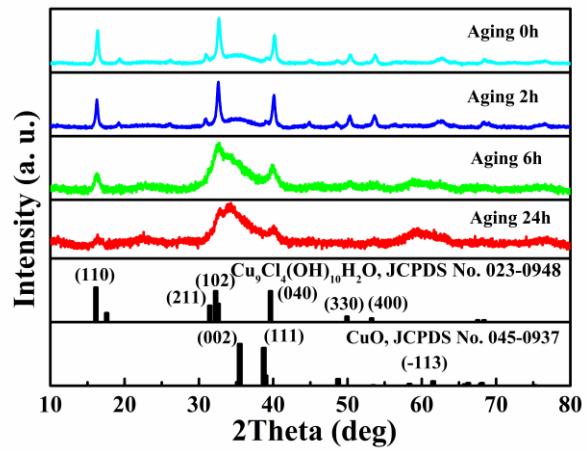


Figure S5. XRD patterns of the precursor before hydrothermal treatment at different aging times.

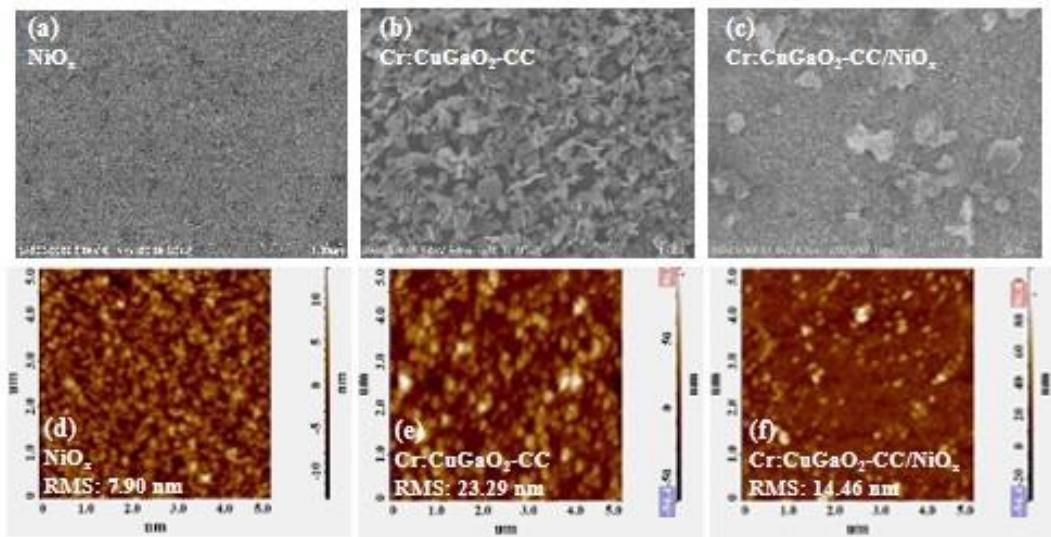


Figure S6. SEM (a)  $\text{NiO}_x$ , (b)  $\text{Cr}:\text{CuGaO}_2\text{-CC}$ , and (c)  $\text{Cr}:\text{CuGaO}_2\text{-CC}/\text{NiO}_x$  hybrid film, respectively. AFM image of (d)  $\text{NiO}_x$ , (e)  $\text{Cr}:\text{CuGaO}_2\text{-CC}$ , and (f)  $\text{Cr}:\text{CuGaO}_2\text{-CC}/\text{NiO}_x$  hybrid film, respectively.

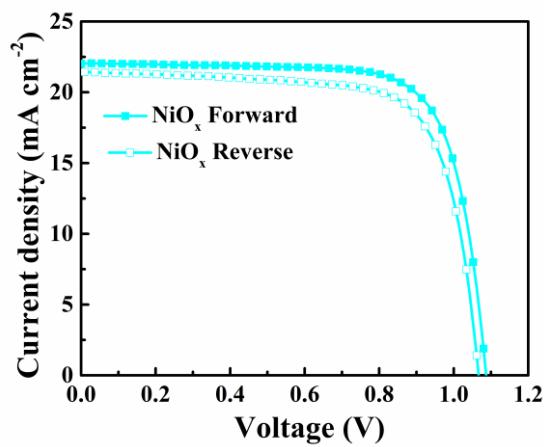


Figure S7.  $J$ - $V$  characteristics of devices extracted from forward and reverse sweeping based on NiO<sub>x</sub> HTL.

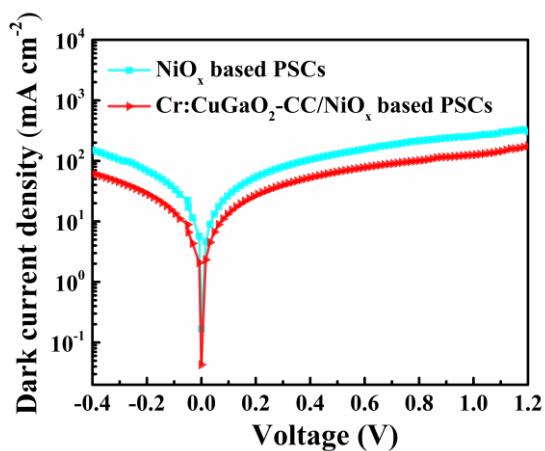


Figure S8. Dark current curves of the devices with  $\text{NiO}_x$  and  $\text{Cr}:\text{CuGaO}_2\text{-CC}/\text{NiO}_x$  HTL, respectively.

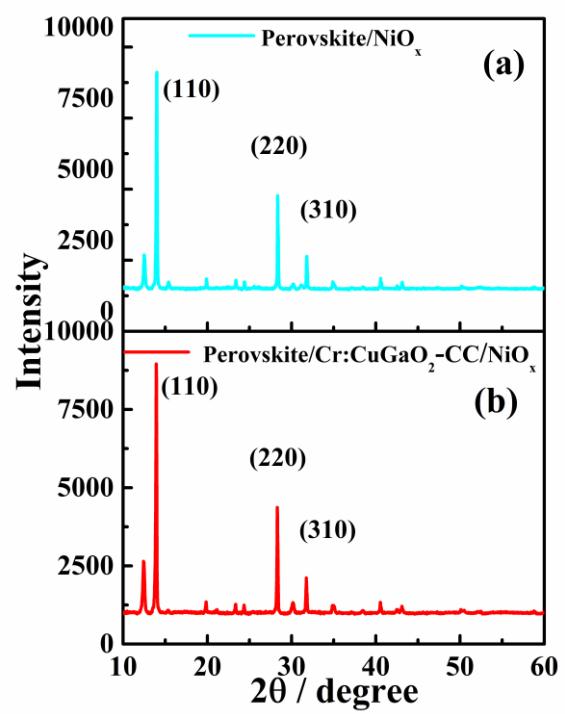


Figure S9. XRD patterns of perovskite crystals growth on (a)  $\text{NiO}_x$  and (b) Cr: $\text{CuGaO}_2$ -CC/ $\text{NiO}_x$  HTL, respectively.

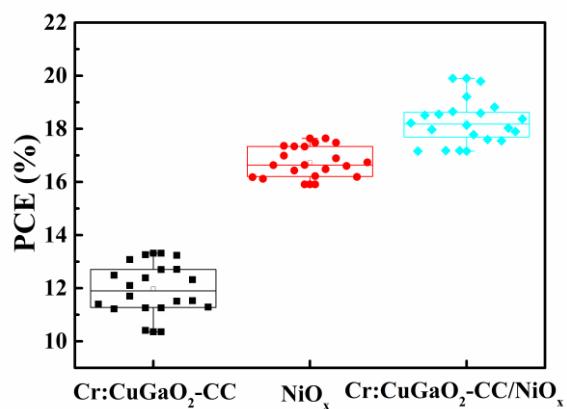


Figure S10. PCE histogram of 20 pristine Cr:CuGaO<sub>2</sub>-CC, NiO<sub>x</sub> and Cr:CuGaO<sub>2</sub>-CC/NiO<sub>x</sub> HTL based PSC devices.

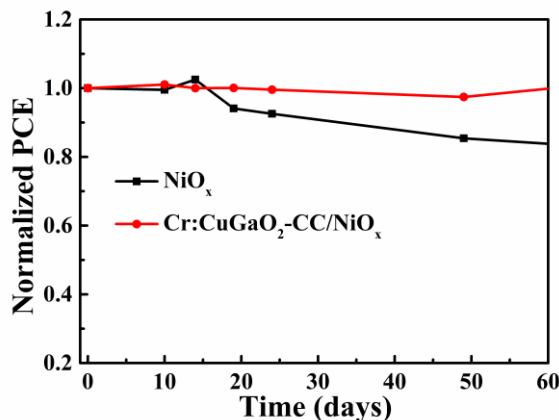


Figure S11. The storage stability of PSCs based on NiO<sub>x</sub> and Cr:CuGaO<sub>2</sub>-CC/NiO<sub>x</sub> HTL.

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