## Electronic Supplementary Information for

## Oxygen-induced degradation in AgBiS<sub>2</sub> nanocrystal solar cells

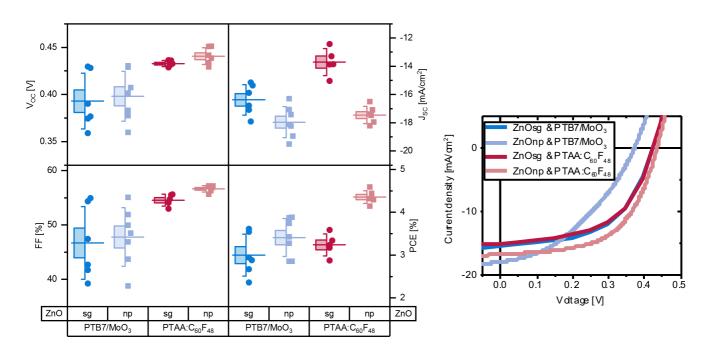
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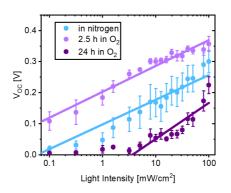
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- Fig. S1 Photovoltaic parameters after two days dark storage of devices with four different combination of extraction layers.
- Fig. S2 Light-intensity-dependent measurements of the V<sub>OC</sub> of a ZnOsg & PTAA:C<sub>60</sub>F<sub>48</sub> AgBiS<sub>2</sub> NC SC.
- Fig. S3 Transient absorption spectra for degrading AgBiS<sub>2</sub> films and their normalised kinetics.
- Fig. S4 Flux dependent transient absorption
- Fig. S5 Transient absorption spectra for pristine and degraded AgBiS2 NC devices with different combination of extraction layers.
- Table S1 Atomic percentages of pristine, 30 nm thick AgBiS<sub>2</sub>-TMAI NC film on a glass/gold substrate, extracted from Fig. 2.
- Fig. S6 FTIR measurements on TMAI and OA capped AgBiS<sub>2</sub> NCs.
- Fig. S7 XRD measurements of pristine and 24h, 20% oxygen and light degraded, AgBiS<sub>2</sub>-TMAI NC films.
- Fig. S8 Microscope images of the silver electrode of AgBiS<sub>2</sub> NC SCs.
- Fig. S9 Atomic force microscopy (AFM) micrographs of two different ZnO configurations.
- Fig. S10 Absorption measurements during oxygen degradation of AgBiS<sub>2</sub> NCs on ZnOsg and np.
- Fig. S11 XPS data for degraded AgBiS<sub>2</sub> NCs deposited on ZnOsg and np.
- Fig. S12 EDX measurement of a aggregates appearing on the AgBiS<sub>2</sub> NC films deposited on a ZnOnp layer.
- Fig. S13 XPS measurements of Ag electrodes of degraded AgBiS<sub>2</sub> NC solar cells.
- Fig. S14 Environmental gas stability for ZnOnp/AgBiS2/PTAA:C60F48 devices under continuous 1 sun irradiation.
- Fig. S15 J<sub>SC</sub> evolution in dry air for different preconditions for ITO/ZnOsg/AgBiS<sub>2</sub>-TMAI/PTAA:C<sub>60</sub>F<sub>48</sub>/Ag devices.

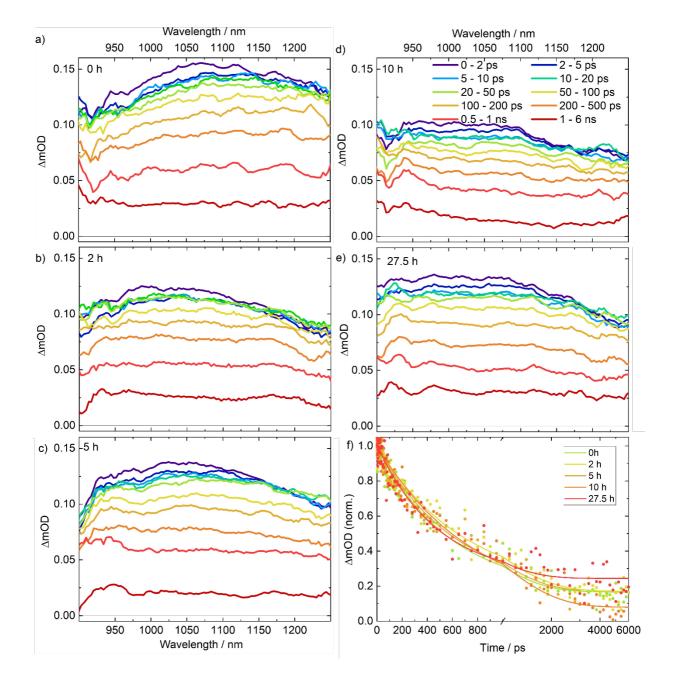
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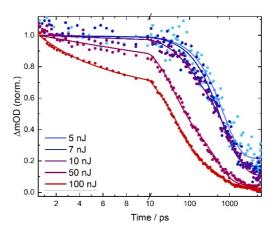
**Fig. S1** left: Photovoltaic paramters after two days of dark storage, measured with 1 sun intensity for the four different comination of extraction layers and on the right: the *JV*-curves of the best performing devices for each case.



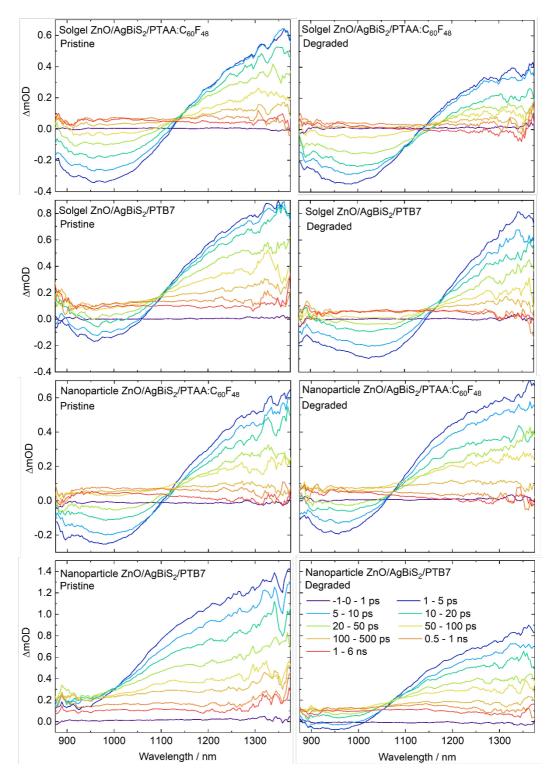
**Fig. S2** Light-intensity-dependent measurements of the  $V_{OC}$  of a ZnOsg & PTAA:C<sub>60</sub>F<sub>48</sub> AgBiS<sub>2</sub> NC SC. The first assessment is performed in nitrogen. Afterwards 20% oxygen are added to the gas flow and in the denoted time frames the second and third measurement are conducted.



**Fig. S3** a-e) transient absorption spectra for neat AgBiS<sub>2</sub> films at increasing extents of degradation, following excitation with a 700 nm pump pulse. f) Normalised kinetics averaged across PIA region for each film with monoexponential fits shown as solid lines.



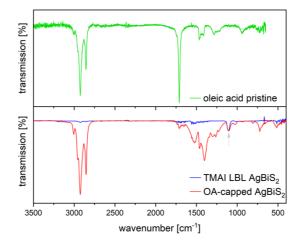
**Fig. S4** Dependence of the normalised near-infrared (NIR) TA kinetics on pump intensity averaged across PIA region with a 700 nm pump wavelength. Solid lines are multiexponential fits.



**Fig. S5** TA spectra for AgBiS<sub>2</sub> devices (pumped at 700 nm) with different hole and electron transport layers, both pristine (left) and following 8 hours of degradation under light and O<sub>2</sub> (right).

**Table S1** Atomic percentages of pristine and 24h, 20% oxygen and light degraded, 30 nm thick AgBiS<sub>2</sub>-TMAI NC film on a glass/gold substrate, extracted from Fig. 2.

Orbital	Atomic	Atomic %
	%(pristine)	(degraded)
C 1s	39.2	43.9
Ag 3d	19.6	15.1
Bi 4f	8.9	7.8
S 2p	12.1	5.5
I 3d	7.4	4.7
O 1s	11.6	20.2
Au 4f	1.2	2.9



## Fig. S6 FTIR measurements on TMAI and OA capped AgBiS<sub>2</sub> NCs. FTIR of OA is provided as reference.

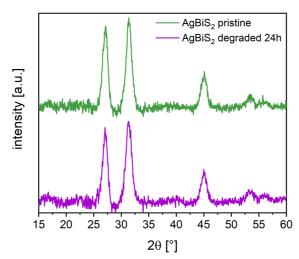
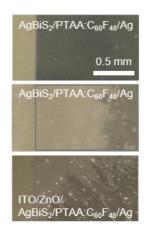


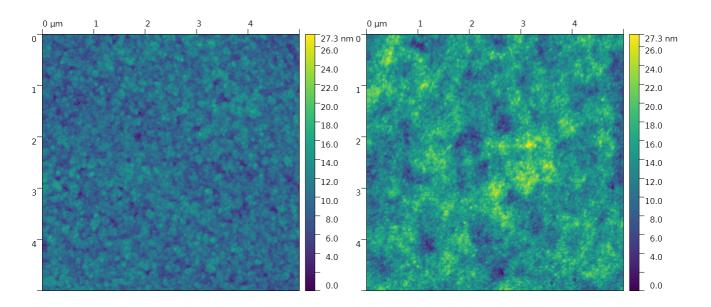
Fig. S7 XRD measurements of pristine and 24h, 20% oxygen and light degraded, AgBiS<sub>2</sub>-TMAI NC films.

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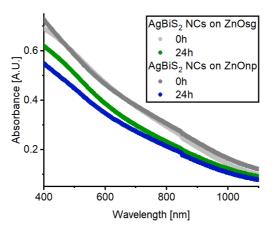
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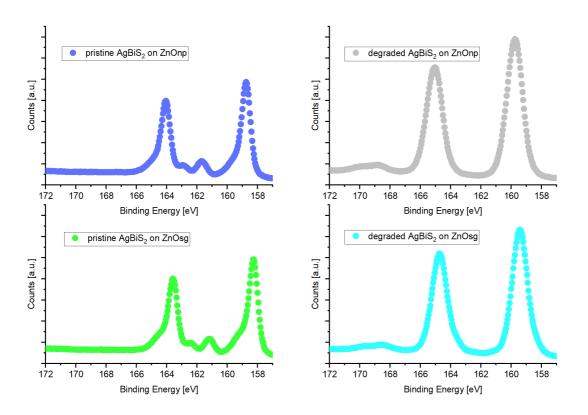
**Fig. S8** Microscope images of the silver electrode (darker area) on AgBiS<sub>2</sub> NC films. Top: pristine state, the lighter part on the left is the uncovered AgBiS<sub>2</sub> NC film. Middle: degraded state after 24 h in oxygen and light, the original electrode extension is outlined. Bottom: degraded state of a full device after 24 h in oxygen and light.



**Fig. S9** Atomic force microscopy (AFM) micrographs of two different ZnO configurations (left: sg, right: np) on glass/ITO.



**Fig. S10** Absorption measurements during degradation of an  $AgbiS_2$  film on top of an ZnOsg and np film. The degradation was performed in dry air and light. Compared to Fig. 5 the absorption loss is enhanced, especially on ZnOnp. The small step at 850nm is caused by a change of grating within the measurement setup.



**Fig. S11** XPS data of the Bi 4f orbital as a measure of the compositional degradation of a layer of  $AgbiS_2$  NCs on ITO/ZnOxx during degradation. Compared to Fig. 5 the degradation after 24 h in dry air and light appears more severe, manifesting in more oxidised species.

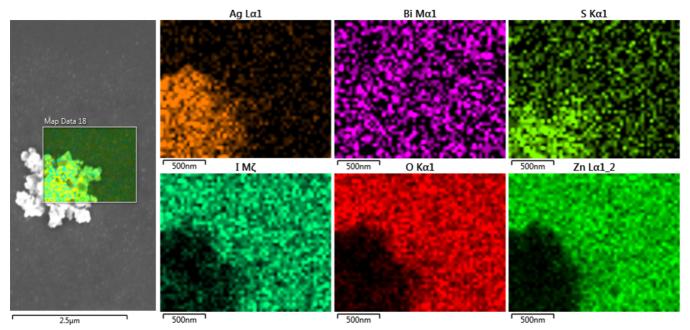


Fig. S12 EDX measurement of a aggregates appearing on the AgBiS<sub>2</sub> NC films deposited on a ZnOnp layer.

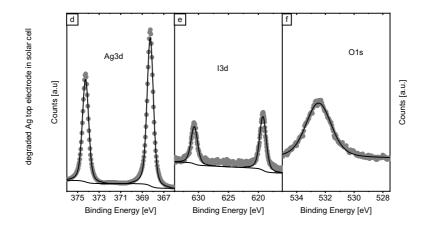
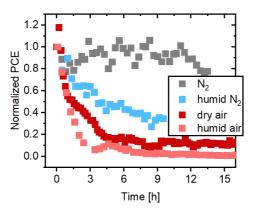
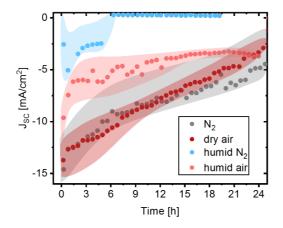


Fig. S13 XPS measurements of Ag electrodes of degraded AgBiS<sub>2</sub> NC solar cells.



**Fig. S14** Environmental stability for  $ZnOnp/AgBiS_2/PTAA:C_{60}F_{48}$  devices under continuous 1 sun irradiation in different atmospheres. The data was normalized to the first measurement value.



**Fig. S15**  $J_{SC}$  evolution in dry air for different preconditions for ITO/ZnOsg/AgBiS<sub>2</sub>-TMAI/PTAA:C<sub>60</sub>F<sub>48</sub>/Ag devices. Preconditioning was carried out for two days in the dark. The transparent shades denote the standard error of the averaged values.

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