

## Solar Cells Reporting Summary

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### ► Experimental design

#### Please check: are the following details reported in the manuscript?

##### 1. Dimensions

|                                          |                                                                        |                                                      |
|------------------------------------------|------------------------------------------------------------------------|------------------------------------------------------|
| Area of the tested solar cells           | <input checked="" type="checkbox"/> Yes<br><input type="checkbox"/> No | This information is available in Supplementary Note. |
| Method used to determine the device area | <input checked="" type="checkbox"/> Yes<br><input type="checkbox"/> No | This information is available in Supplementary Note. |

##### 2. Current-voltage characterization

|                                                                                                                                                                                                |                                                                        |                                                                                                                                                                                                                                               |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Current density-voltage (J-V) plots in both forward and backward direction                                                                                                                     | <input type="checkbox"/> Yes<br><input checked="" type="checkbox"/> No | In the photocatalysis with III-V semiconductor photocathode, a single sweep JE curve from negative to positive potentials has been the common practice, since the scan from the positive to negative potentials can overestimate performance. |
| Voltage scan conditions<br><i>For instance: scan direction, speed, dwell times</i>                                                                                                             | <input checked="" type="checkbox"/> Yes<br><input type="checkbox"/> No | This information is available in Methods section.                                                                                                                                                                                             |
| Test environment<br><i>For instance: characterization temperature, in air or in glove box</i>                                                                                                  | <input checked="" type="checkbox"/> Yes<br><input type="checkbox"/> No | This information is available in Methods section.                                                                                                                                                                                             |
| Protocol for preconditioning of the device before its characterization                                                                                                                         | <input type="checkbox"/> Yes<br><input checked="" type="checkbox"/> No | Preconditioning is not necessary for III-V solar cells and photoelectrodes.                                                                                                                                                                   |
| Stability of the J-V characteristic<br><i>Verified with time evolution of the maximum power point or with the photocurrent at maximum power point; see <a href="#">ref. 7</a> for details.</i> | <input checked="" type="checkbox"/> Yes<br><input type="checkbox"/> No | JE characteristics after PEC stability tests were provided in Supplementary Figs. 14 and 15.                                                                                                                                                  |

##### 3. Hysteresis or any other unusual behaviour

|                                                                           |                                                                        |                                                               |
|---------------------------------------------------------------------------|------------------------------------------------------------------------|---------------------------------------------------------------|
| Description of the unusual behaviour observed during the characterization | <input type="checkbox"/> Yes<br><input checked="" type="checkbox"/> No | No hysteresis or unusual behavior of solar cell was observed. |
| Related experimental data                                                 | <input type="checkbox"/> Yes<br><input checked="" type="checkbox"/> No | No hysteresis or unusual behavior of solar cell was observed. |

##### 4. Efficiency

|                                                                                                                                 |                                                                        |                                                                                                                         |
|---------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|
| External quantum efficiency (EQE) or incident photons to current efficiency (IPCE)                                              | <input type="checkbox"/> Yes<br><input checked="" type="checkbox"/> No | EQE or IPCE measurements were not performed in this study as they are not required to support the claims of this study. |
| A comparison between the integrated response under the standard reference spectrum and the response measure under the simulator | <input type="checkbox"/> Yes<br><input checked="" type="checkbox"/> No | EQE or IPCE measurements were not performed in this study.                                                              |
| For tandem solar cells, the bias illumination and bias voltage used for each subcell                                            | <input type="checkbox"/> Yes<br><input checked="" type="checkbox"/> No | Tandem solar cells were not studied.                                                                                    |

##### 5. Calibration

|                                                                         |                                                                        |                                                   |
|-------------------------------------------------------------------------|------------------------------------------------------------------------|---------------------------------------------------|
| Light source and reference cell or sensor used for the characterization | <input checked="" type="checkbox"/> Yes<br><input type="checkbox"/> No | This information is available in Methods section. |
| Confirmation that the reference cell was calibrated and certified       | <input checked="" type="checkbox"/> Yes<br><input type="checkbox"/> No | This information is available in Methods section. |

|                                                                                                                                                                                               |                                                                        |                                                                                                                                                                                                                                                                                                                                                                                    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Calculation of spectral mismatch between the reference cell and the devices under test                                                                                                        | <input type="checkbox"/> Yes<br><input checked="" type="checkbox"/> No | Calculation of spectral mismatch was not performed as it is not required to support the claims of this study.                                                                                                                                                                                                                                                                      |
| <b>6. Mask/aperture</b>                                                                                                                                                                       |                                                                        |                                                                                                                                                                                                                                                                                                                                                                                    |
| Size of the mask/aperture used during testing                                                                                                                                                 | <input type="checkbox"/> Yes<br><input checked="" type="checkbox"/> No | Mask or aperture was not used during testing as the device performance in this study is not affected by them.                                                                                                                                                                                                                                                                      |
| Variation of the measured short-circuit current density with the mask/aperture area                                                                                                           | <input type="checkbox"/> Yes<br><input checked="" type="checkbox"/> No | Measured short-circuit current density in this study is not affected by the mask/aperture area.                                                                                                                                                                                                                                                                                    |
| <b>7. Performance certification</b>                                                                                                                                                           |                                                                        |                                                                                                                                                                                                                                                                                                                                                                                    |
| Identity of the independent certification laboratory that confirmed the photovoltaic performance                                                                                              | <input type="checkbox"/> Yes<br><input checked="" type="checkbox"/> No | Performance certification was not carried out as it is not required to support the claims of this study.                                                                                                                                                                                                                                                                           |
| A copy of any certificate(s)<br><i>Provide in Supplementary Information</i>                                                                                                                   | <input type="checkbox"/> Yes<br><input checked="" type="checkbox"/> No | Performance certification was not carried out.                                                                                                                                                                                                                                                                                                                                     |
| <b>8. Statistics</b>                                                                                                                                                                          |                                                                        |                                                                                                                                                                                                                                                                                                                                                                                    |
| Number of solar cells tested                                                                                                                                                                  | <input checked="" type="checkbox"/> Yes<br><input type="checkbox"/> No | This information is available in Methods section.                                                                                                                                                                                                                                                                                                                                  |
| Statistical analysis of the device performance                                                                                                                                                | <input type="checkbox"/> Yes<br><input checked="" type="checkbox"/> No | PEC measurements in Figs. 2a, 3a, 4a, 4b, 4f involve the comparison of electrode performance for multiple samples prepared by different processing conditions, where representative data from 2 or 3 sets of samples were reported for each figure. Statistical analysis among different sample batches is not required to support the conclusion of these comparison experiments. |
| <b>9. Long-term stability analysis</b>                                                                                                                                                        |                                                                        |                                                                                                                                                                                                                                                                                                                                                                                    |
| Type of analysis, bias conditions and environmental conditions<br><i>For instance: illumination type, temperature, atmosphere humidity, encapsulation method, preconditioning temperature</i> | <input checked="" type="checkbox"/> Yes<br><input type="checkbox"/> No | Long-term stability analysis of photoelectrodes during the hydrogen evolution reaction was included in the main text (Figure 4).                                                                                                                                                                                                                                                   |