Supplementary Materials for

## Enhanced photo-response performance of Cu<sub>2</sub>O-based graded heterojunction optoelectronic devices with Ga<sub>2</sub>O<sub>3</sub> buffer layer

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Figure S1. The AFM 3D images of various  $Ga_2O_3$  films deposited on ITO glass with different oxygen pressure. a)10<sup>-4</sup> Pa, b)1 Pa, c)5 Pa, and d)20 Pa.



Figure S2. Top-view SEM images of  $Ga_2O_3$  films deposited at various oxygen pressure.



Figure S3. KPFM image of a HOPG flake.



Figure S4. a) Absorption spectra b) X-ray diffraction spectra of  $Cu_2O$  films deposited at various oxygen pressure.



**Figure S5.** Current density-voltage curves measured under an AM 1.5G solar simulator of the photovoltaic device architectures of ITO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O/Au using various oxygen pressure prepared Ga<sub>2</sub>O<sub>3</sub>.



**Figure S6.** Current-voltage characteristics for electrical conductance comparison of devices with a structure of In/Ga<sub>2</sub>O<sub>3</sub>/In using various oxygen pressure prepared Ga<sub>2</sub>O<sub>3</sub>.



**Figure S7.** Current density-voltage curves measured under an AM 1.5G solar simulator of the various device architectures. (ITO/ZnO/Cu<sub>2</sub>O/Au; ITO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O/Au; ITO/ZnO/Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O/Au)



Figure S8. The electronic band alignment of the  $ITO/ZnO/Cu_2O$  and  $ITO/ZnO/Ga_2O_3/Cu_2O$  heterojunction, showing a stepped arrangement by incorporating PLD Ga\_2O\_3.



**Figure S9**. a-c) The temporal photoresponse of devices with structure of  $ITO/Ga_2O_3/Cu_2O/Au$  at 0 bias voltage, during multiples dark/light cycles of approximately 2.5 s.  $Ga_2O_3$  films were deposited at different oxygen pressure.

|   | $Jsc (mA cm^{-2})$ | Voc (V) | FF    | PCE (%) |
|---|--------------------|---------|-------|---------|
| ZnO/ Cu <sub>2</sub> O                                  | 2.88               | 0.31    | 0.426 | 0.38    |
| Ga <sub>2</sub> O <sub>3</sub> /Cu <sub>2</sub> O       | 4.13               | 0.35    | 0.456 | 0.66    |
| ZnO /Ga <sub>2</sub> O <sub>3</sub> / Cu <sub>2</sub> O | 4.99               | 0.34    | 0.554 | 0.94    |

Table S1. Parameters of the solar cells fabricated with different architectures.

Table S2. Electrical properties of Cu<sub>2</sub>O prepared on glass at various oxygen pressure.

| Pressure (Pa) | Hall Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ) | Carrier Density (cm <sup>-3</sup> ) |
|---------------|--|-------------------------------------|
| 0.1           | 3.84*10-1  | 2.31*10 <sup>18</sup>               |
| 0.5           | 4.04*10-1  | 8.84*1017                           |
| 1             | $1.31^{*}10^{0}$   | 2.22*10 <sup>16</sup>               |
| 1.5           | 9.57*10-1  | 8.52*1015                           |