**Electronic supplementary material.** 



**Fig. SI1.** Evolution of the crystallite size as a function of the annealing temperature for CuO photoelectrodes.



**Fig. SI2.** (a) XRD patterns for dense (blue) and mesoporous (orange) photoelectrodes (\* signs indicate underlying  $SnO_2$  and O signs correspond to CuO phase). (b) SEM images for dense (1) and mesoporous (2) photoelectrodes (Inset. Cross-section of the respective photoelectrodes). Annealing temperature is 400°C in air for 20 min. The sol concentration was 0.3 mol.L<sup>-1</sup>.



**Fig. SI3.** UV–visible diffuse reflectance spectra for dense (blue) and mesoporous (orange) photoelectrodes annealed at 400°C in air for 20 min. The sol concentration was 0.3 mol.L<sup>-1</sup>.



**Fig. SI4.** (a) XRD patterns for 400-CuO photoelectrodes before (blue) and after (orange) photoelectrochemical testing (\*: SnO<sub>2</sub>, O: CuO and  $\Delta$ : Cu phases), SEM images (b) of *protected* (1) and *unprotected* (2) zones for dense photoelectrodes after photoelectrochemical testing. Red arrows indicate the preferential zones where Cu dissolution is observed. Annealing temperature is 400°C under air for 20 min. The sol concentration was 1.5 mol.L<sup>-1</sup>.



**Fig. SI5.** (a) XRD patterns for 400-CuO bare photoelectrodes (C =  $1.5 \text{ mol.L}^{-1}$ ) before and after the deposition of *n*-TiO<sub>2</sub> layers (\*: SnO<sub>2</sub>, O: CuO and  $\diamond$ : TiO<sub>2</sub>, n=1-3), (b) SEM images of CuO bare photoelectrodes (1) and protected CuO photoelectrodes by 2 TiO<sub>2</sub> layers (2). Annealing temperature is 500°C under air for 1 h. The sol concentration was 1.5 mol.L<sup>-1</sup> for CuO and 0.3 mol.L<sup>-1</sup> for TiO<sub>2</sub>.



**Figure SI6.** Absorbance as function of the wavelength for 2-layers  $TiO_2$  films (orange), 2-layers CuO films (green) and  $TiO_2$ -protected CuO films (blue).



**Figure SI7.** Nyquist plots of electrochemical impedance spectra for CuO (red) and CuO/TiO<sub>2</sub> (blue) in light conditions at pH = 6 and 0 V vs. RHE. Measurements from 200 kHz to 0.1 Hz.

Sample	CuO	CuO/TiO <sub>2</sub>
Photocurrent (mA/cm <sup>2</sup> ), $t = 200s$	- 0.94	- 0.5
Photocurrent (mA/cm <sup>2</sup> ), $t = 600s$	- 0.87	- 0.5
Stability (%) J <sub>600</sub> /J <sub>200</sub>	92	100

Table. S1. Photocurrent values of 400-CuO with and without protective TiO<sub>2</sub> layer, 0 V vs. RHE for pH=7-8.