Supporting Information to

Cu Nanoparticles Enables Plasmonic-Improved Silicon Photovoltaic Devices

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S1. Spectral Confirmation of the Oxidation of the Cu NPs.

Two representative extinction spectra of the Cu NPs obtained at different reaction times under nitrogen flux were baseline corrected. This procedure eliminated the spectral contribution of Cu interband transition, and allowed a better observation of the Cu SPR and of the Cu_2O layer absorption peaks. The decomposed spectra are shown in Figure S1.
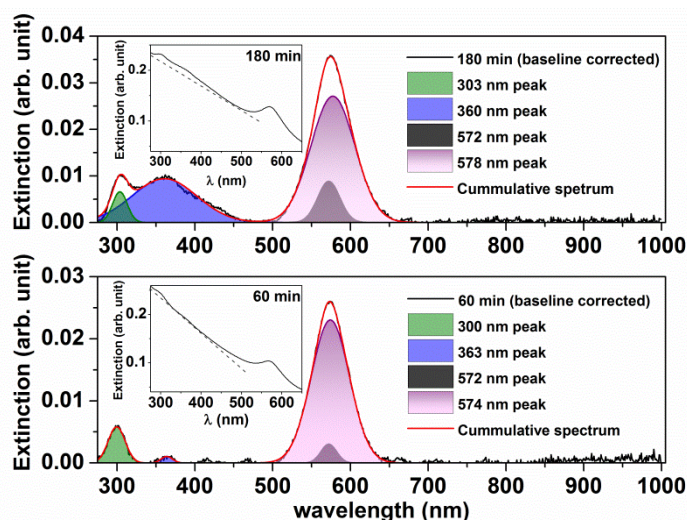

Figure S1. Extinction spectra of Cu NPs in aqueous solution at different reaction times (60 and 180 minutes), baseline corrected and peaks decomposed (original extinction spectra inset).

The figures inset show a representative dashed line under the peaks of interest of the copper (I) oxide to emphasize the presence of absorption peaks. The spectrum after 60 minutes of synthesis presents a peak at 300 nm and a very low intense band at 360 nm, assigned to the band-to-band transition of nanocrystalline Cu_2O,[1] and a strong band at approximately 574 nm (sum of 572 and 574 nm bands) that correspond to the Cu NPs surface plasmon resonance.[2] A clear the intensification of

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the 360 nm peak (50-fold increase) is observed in the spectrum of the Cu NPs after 180 minutes of reaction. This increase can be assigned to a thicker oxide layer over the Cu NPs,[3] confirming the structure suggested in the literature (Cu@Cu$_2$O). The thicker oxide layer causes broadening and the red-shift of the Cu surface plasmon peak from 574 nm to 578 nm, moving the SPR further away from the Cu interband transition.

S2 Surface Plasmon Resonance of Cu NPs Immobilized in the PVs

The difference between the reflection spectra of Si PVs without and with Cu NPs is shown in Figure S2.
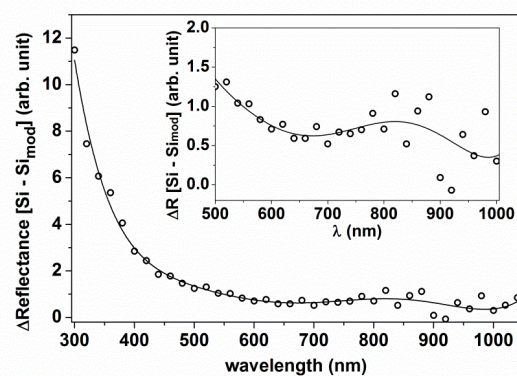
Figure S2. Difference spectrum between the reflection of a PV surface without Cu NPs and with Cu NPs (From Figure 3(A)).

Figure 3 (A) of the manuscript showed that the presence of the NPs decrease the amount of reflected light from the Si PV surface in the whole spectral range investigated. The difference between the reflection spectra of Si PVs without and with Cu NPs shows then a positive response that should correlate with the extinction characteristics of the immobilized Cu NPs. Figure S2 shows an intense extinction in the wavelength region below 500 nm, also discussed in the manuscript, which should be associated to the Cu interband transition. This result agrees with Figure 3 (B) of the manuscript (ΔEQE_{ref}), where an intense damping in wavelengths below 500 nm is observed. It is interesting to note that the Cu NPs modified Si PV presents positive extinction in all visible and NIR range. The extinction at those wavelengths correlates to an increase in solar cell efficiency, suggesting that it is dominated by light scattering into the PV. A (weak) surface plasmon peak is observed at 850 nm (zoomed in Figure S2 inset).

S3 Equivalence between the EQE and Jsc measurements.

EQE and Jsc are proportional measures and yield the same information, as the following equations:

$$EQE = \frac{\text{number of generated electons}}{\text{number of incident photons}} = \frac{J_{sc} \times h \times c}{\lambda \times P_{in}} \qquad \text{Equation 1}$$

$$\Delta EQE_{rel} = \frac{EQE_{final} - EQE_{inicial}}{EQE_{inicial}} = \frac{(Jsc_{final} - Jsc_{inicial}) \times \left(\frac{hc}{\lambda P_{in}}\right)}{Jsc_{inicial} \times \left(\frac{hc}{\lambda P_{in}}\right)} \qquad \text{Equation 2}$$

$$\Delta Jsc_{rel} = \frac{Jsc_{final} - Jsc_{inicial}}{Jsc_{inicial}} \qquad \text{Equation 3}$$

In our case, the EQE were performed at the Day4 Energy (using certified equipment from this commercial solar cell provider) and the Jsc measured at the University of Victoria. The consistence between different techniques from different places provided an additional degree of confidence on the results presented in the manuscript.

S4 Standard Characterization of All the Devices Relevant to this Manuscript.

The J-V and power curves under white light irradiation are shown in Figure S3. The respective surface coverage is indicated in each figure.
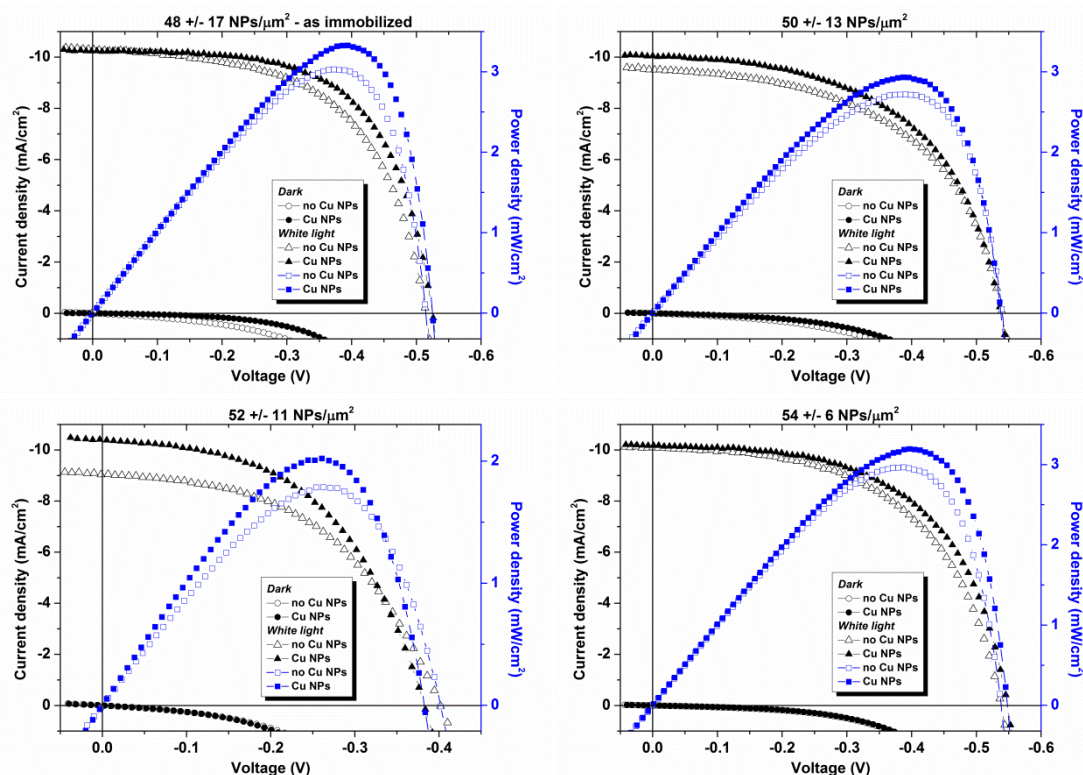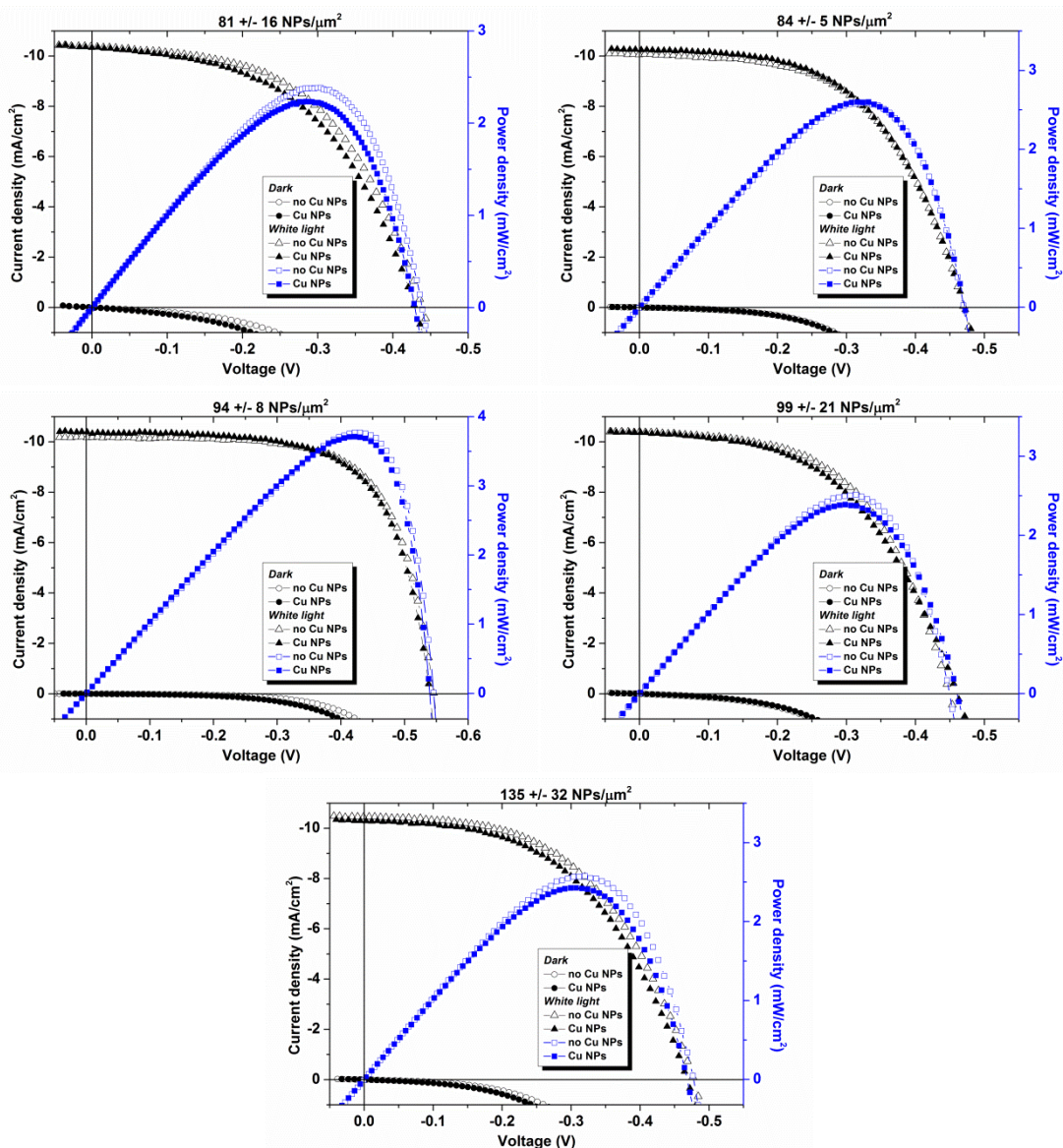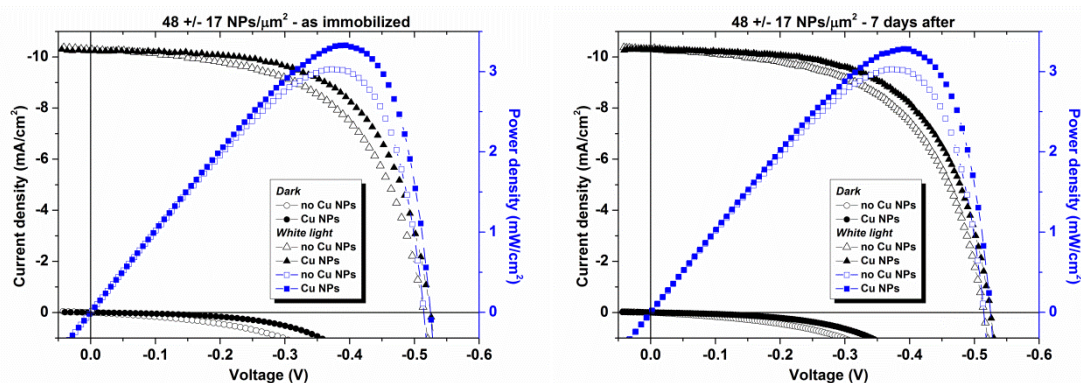
Figure S3. J-V and power curves for PVs with different surface coverage of Cu NPs.

S5 Time-Dependent Deterioration of the Performance of the PV cell Coated with Cu NPs.

The J-V and power curves of the plasmonic PV as modified and after 7 days prepared are shown in Figure S4.

Figure S4. J-V and power curves to the Si PV with surface coverage of 48 NPs/µm^2 Cu NPs as immobilized and after 7 days preparation.

The modified Si PV as immobilized Cu NPs presented 9.9 % of power increased compared to the Si PV without Cu NPs. The same modified Si PV after 7 days exposed to air presented 8.4 % power increased (Figure S4). Although the power efficiency after 7 days exposed to air suffered a decreased of 1.5 % due to the low stability of the Cu NPs and possible plasmon intensity losses, it was still observed an improvement on the Si PV efficiency compared to the Si PV without Cu NPs, confirming that the Cu$_2$O layer slow the oxygen diffusion to the Cu core as discussed in the manuscript. The main objective of the present work was to systematically probe the plasmon effect of Cu NPs on Si PVs, and thus no systematic studies on the cell stability were carried out.

References

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