# ZnO-CuO Backbone-Branch Heterostructure for High-Efficiency Organic-Inorganic Hybrid Perovskite Solar Cells


***Kichang Jung[1,3], Taehoon Lim[2,3], Alfredo A. Martinez-Morales[3]***

*[1]Department of Chemical and Environmental Engineering,*
*[2]Materials Science and Engineering Program,*
*[3]Southern California Research Initiative for Solar Energy, College of Engineering*
*Center for Environmental Research and Technology University of California, Riverside, California 92521*
*(alfmart@ece.ucr.edu)*


## Abstract


Population growth has led to an unsustainable demand in energy consumption. Due to its renewable, sustainable, and clean nature, solar energy remains as one of the most promising sources of energy. Dye-sensitized solar cells (DSSCs) and perovskite solar cells (PSCs) have emerged as an attractive alternate technology to silicon-based devices, due to their ease of fabrication, low material cost, and versatility of application. However, the absorption materials in these solar cells cannot absorb near-infrared (NIR) light, which inherently limits their efficiency. In this work, CuO is used as a secondary absorption layer to utility NIR light for improving device efficiency. ZnO nanorods (NRs) on fluorine-doped tin oxide (FTO) substrate are synthesized by chemical vapor deposition. CuO is synthesized on ZnO NRs by thermal oxidation. Properties of the synthesized materials are characterized by SEM, XRD, and UV-Vis-NIR photospectroscopy.


## Background

### ❑ Photovoltaic Principle

Solar cells consist of two electrodes, an absorber layer, an electron and a hole transport layer (ETL and HTL, respectively). In short, electrons are excited at the absorber layer by incoming photons. The excited electrons are collected by the negative electrode. The wavelength range of the absorbed light depends on the band gap of the absorber material being utilized.

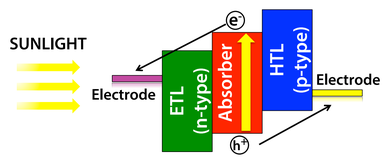


**Figure 1**. Schematic of solar cell device

### ❑ Electron-Transfer Processes

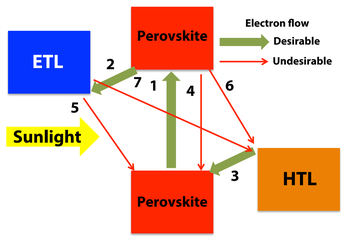


**Figure 2**. Schematic of electron-transfer processes

For higher performance of solar cell devices, processes 4-7 must be minimized, while 1-3 should be maximized.

### ❑ Limitation of Perovskite

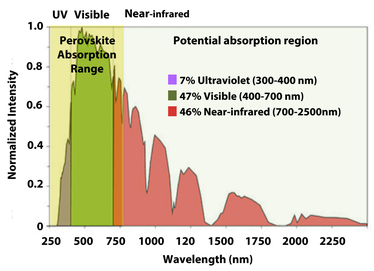


**Figure 3**. Solar spectrum distribution

Non-absorption of near-infrared light limits efficiency of perovskite-based solar cells.

## Research Objective

### ❑ Overall Goal

Improve the conversion efficiency of perovskite solar cells by using novel heterostructure photoelectrode and modified absorber.

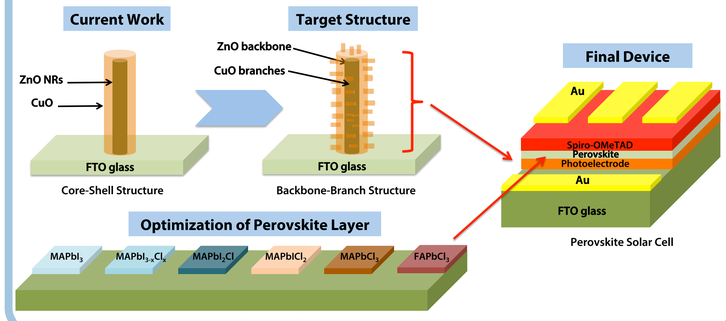


**Figure 4**. Current and proposed research work

## Experimental Process & Results

### ❑ ZnO NRs Synthesis on FTO glass

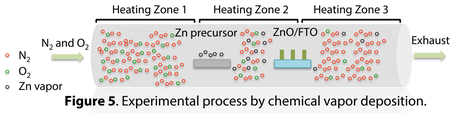


**Figure 5**. Experimental process by chemical vapor deposition.

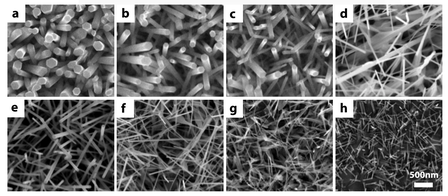


**Figure 6**. SEM images of ZnO NRs synthesized with various gas ratio.

**Table 1**. ZnO NRs diameter with respect to process gas ratio

| Sample | $N_2$ (sccm) | $O_2$ (sccm) | Gas ratio ($O_2/N_2$) | Diameter (nm) |
|---|---|---|---|---|
| a | 90 | 10 | 0.100 | 175 |
| b | 92 | 8 | 0.080 | 140 |
| c | 94 | 6 | 0.060 | 91 |
| d | 96 | 4 | 0.040 | 45 |
| e | 98 | 2 | 0.020 | 63 |
| f | 99 | 1 | 0.010 | 31 |
| g | 100 | 0.5 | 0.005 | 36 |
| h | 100 | 0.3 | 0.003 | 24 |

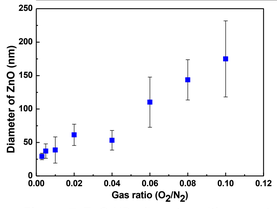


**Figure 7**. ZnO NRs diameter with respect to process gas ratio

Figure 6 shows that the diameter of ZnO NRs increase with higher oxygen ratio during CVD synthesis (from 24 to 175 nm). This result indicates that the diameter of ZnO NRs can be controlled during growth.

### ❑ CuO Synthesis on FTO glass

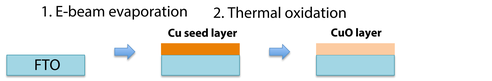


**Figure 8**. CuO Synthesis by thermal oxidation

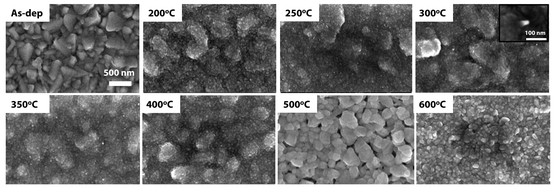


**Figure 9**. SEM images of Cu-oxide compound on FTO glass with various thermal oxidation process temperature.

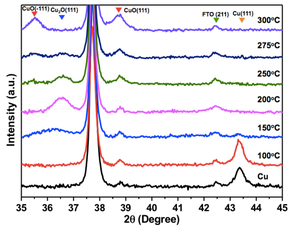


**Figure 10**. X-ray diffraction pattern for Cu-oxide compounds of FTO glass.

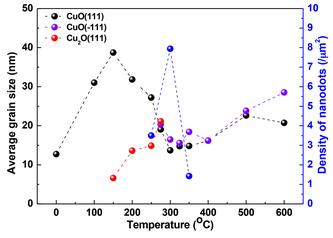


**Figure 11**. Average grain size and nanodot density of Cu-oxide compounds.

Cu-oxide compounds nanodots are synthesized with small grain size at thermal oxidation temperature ranging from 250 °C to 350 °C

- Scherrer's Equation

$$\tau = \frac{k\lambda}{\beta cos\theta}$$

τ : Average grain size θ: Bragg angle
k: Shape factor (0.9)
λ: X-ray wavelength
β: Full half width at half maximum

### ❑ ZnO-CuO Core-Shell Synthesis


**Figure 12**. SEM characterization of CuO obtained on ZnO NRs with/without HCl pre-treatment before thermal oxidation.

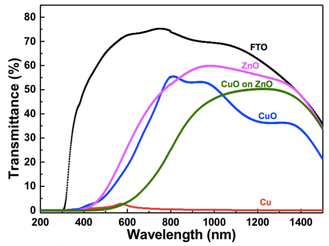


**Figure 13**. Transmittance spectra for ZnO-Cu, ZnO-CuO and CuO in the ultra violet, visible, and near-infrared light range.

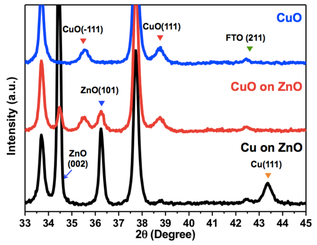


**Figure 14**. X-ray diffraction pattern for ZnO-Cu, ZnO-CuO and CuO.

The transmittance spectra shows CuO on ZnO NRs can absorb near-infrared light with wavelength longer than 800 nm. Therefore, CuO on ZnO NRs can be used as a secondary absorption layer in perovskite solar cells to widen the absorption range towards the near-infrared light.

**Table 2**. Energy-dispersive X-ray spectroscopy (EDX) results for ZnO-Cu, ZnO-CuO and CuO.

| CuO | | CuO on ZnO | | Cu on ZnO | |
|---|---|---|---|---|---|
| Cu | 32.8 | Cu | 29.4 | Cu | 41.9 |
| Zn | None | Zn | 18.0 | Zn | 34.0 |
| O | 51.1 | O | 48.6 | O | 24.1 |
| Sn | 16.1 | Sn | 4.0 | Sn | None |

## Conclusion

In this work, we have successfully synthesized ZnO-CuO nanoscale, core-shell structures by using a two-step synthesis process; 1) chemical vapor deposition, and 2) thermal oxidation. From the XRD results, crystallinity of ZnO and Cu-oxide compounds are determined, and the grain size of Cu-oxide compounds are calculated by using Scherrer's equation. The diameter of ZnO NRs increases with higher oxygen ratio. Cu-oxide compound nanostructures are synthesized when the grain size of the compounds is small. In order to synthesize many nanostructures of CuO, we will research advanced thermal oxidation method (two-step method). In the future, perovskite solar cells (PSCs) using synthesized ZnO-CuO backbone-branch structure, as a photoelectrode, will be fabricated. Performance of the PSCs using various photoelectrodes structure will be compared to understand the effect of CuO material as a branch on ZnO.

## Reference


[1] http://ce.construction.com/article_print.php?L=68&C=790
[2] Martin A. Green, Anita Ho-Baillie & Henry J. Snaith, *Nature* **8**, 506-514 (2014)
[3] Giles E. Eperon, Victor M. Burlakov, Pablo Docampo, Alain Goriely & Henry J. Snaith, *Adv. Funct. Mater.* **24**, 2151-157 (2014)
[4] Liang Li, Tianyou Zhai, Yoshio Bando & Dmitri Golberg, *Nano Energy* **1**, 91–106 (2012)
[5] Henry J. Snaith, *J. Phys. Chemx. Lett.* 4, 3623–3630 (2013)


## Acknowledgements


This research was partially funded by the University of California Advanced Solar Technologies Institute (UC Solar).