Supporting Information

Understanding the Improved Stability of Hybrid Polymer Solar Cells Fabricated with Copper Electrodes

B. Reeja-Jayan and Arumugam Manthiram^{*} Materials Science and Engineering Program The University of Texas at Austin Austin, TX 78712

E-mail: <u>rmanth@mail.utexas.edu</u>.

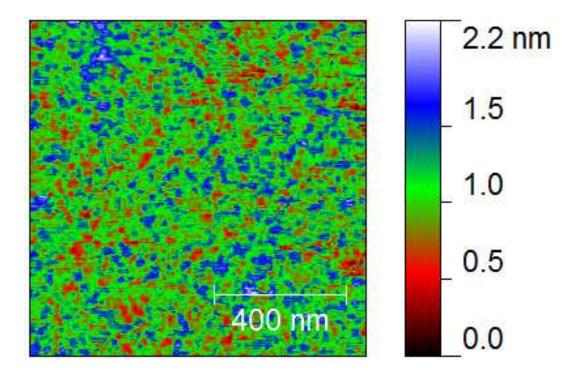


Figure S1. AFM image of sol-gel derived TiO₂ film.

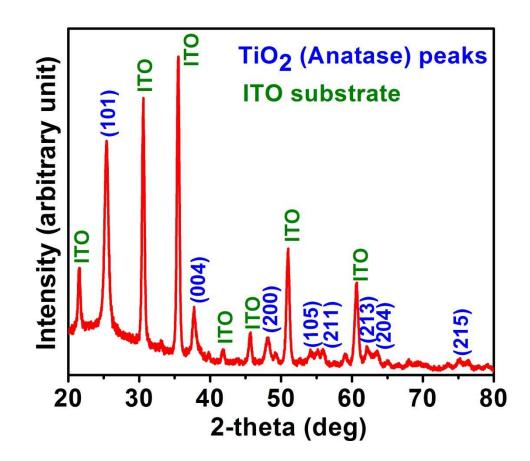


Figure S2. GIXRD pattern of sol-gel derived TiO₂ film.

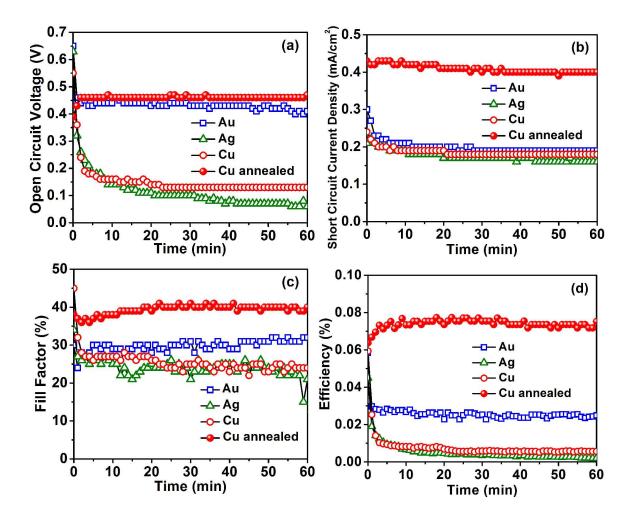


Figure S3. Variation of (a) V_{oc} , (b) J_{sc} , (c) FF, and (d) efficiency during continuous illumination in air.

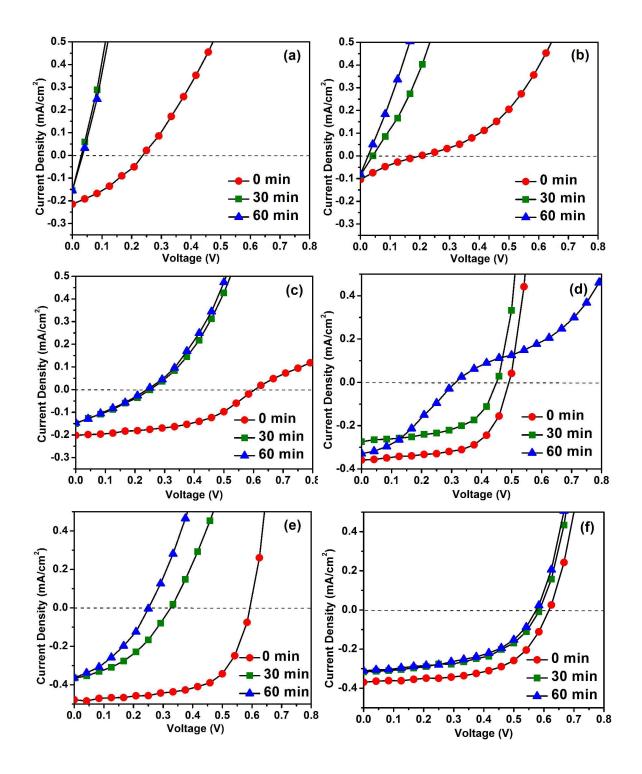


Figure S4. J-V curves during continuous illumination in argon for cells based on (a) Au, (b) Ag, (c) Cu, (d) annealed Au, (e) annealed Ag, and (f) annealed Cu electrodes.

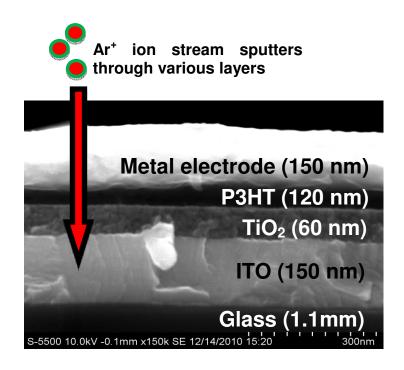


Figure S5. Cross-sectional SEM image of a P3HT-TiO₂ hybrid solar cell used to calibrate Ar^+ beam sputter rate.

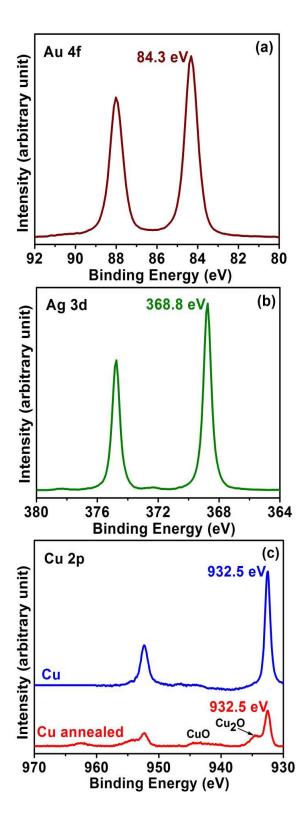


Figure S6. XPS spectra of the metal electrode surface: (a) Au 4f, (b) Ag 3d, and (c) Cu 2p. Binding energy values are tabulated in Table S1.

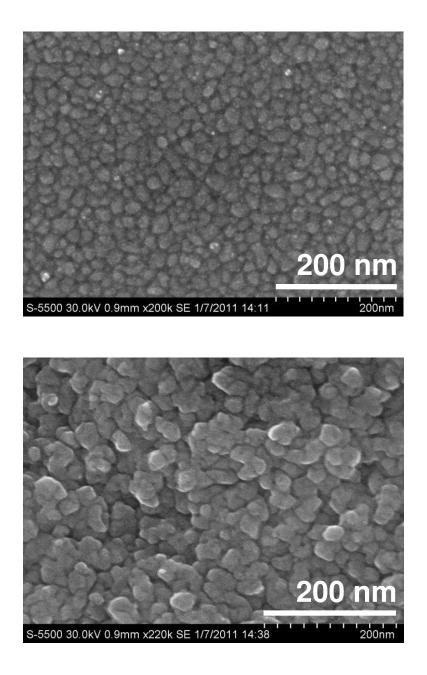


Figure S7. SEM image of the surface of (a) Cu electrode and (b) annealed Cu electrode.

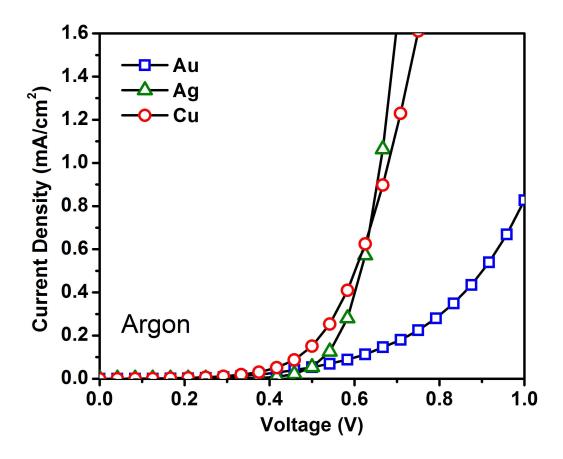


Figure S8. Dark J-V characteristics of P3HT-TiO2 hybrid solar cells after illumination.

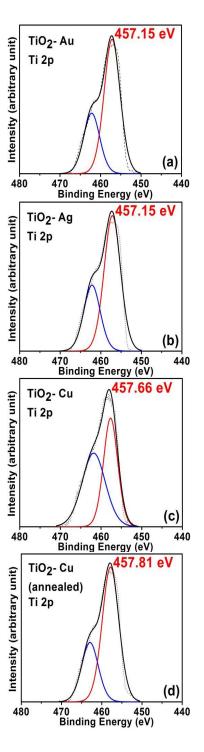


Figure S9. XPS Ti 2p spectra of P3HT-TiO₂ interface in case of (a) Au, (b) Ag, (c) Cu, and (d) annealed Cu electrode. Positive shift in binding energy is observed from top to bottom. See Table S2.

Advantages of Cu Electrode. Recent reports have demonstrated the utility of colloidal Cu nanoparticle inks as low-cost, printable electrodes for solution-deposited thin film devices like transistors (41). The oxidation of Cu nanoparticles was controlled by adjusting the molecular weight of poly(N-vinylpyrrolidone) capping molecules. Copper also presents other advantages like corrosion resistance, ease of fabrication, abundant availability, and overall cost-effectiveness. Encouraged by these reports, we have also tested these Cu electrodes in solar cells in which the P3HT layer was replaced by a blend of P3HT and C₆₁-butyric acid methyl ester (PCBM). These cells were fabricated following the fabrication steps and blend concentrations reported in the literature (42). Table S3 reveals that the photovoltaic efficiencies increase on adding PCBM. Illuminated J-V curves in Figure S10 show that the as-prepared Cu cells exhibit improved photovoltaic performance compared to both the Au- and Ag-based cells. This suggests that in addition to the stability improvement of the P3HT-TiO₂ hybrid solar cells, which is the primary focus of this paper, Cu can also be pursued as a low-cost alternative to the noble metal electrodes used in other types of polymer solar cells.

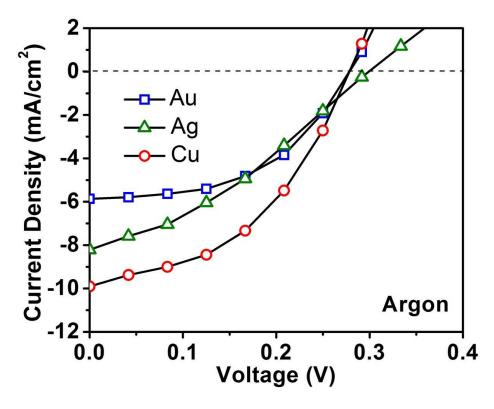


Figure S10. Illuminated J-V characteristics of P3HT-PCBM blend solar cells fabricated with different metal electrodes. The photovoltaic parameters are summarized in Table S3.

| Electrode Metal | Binding Energy (eV) |
|--------------------------|------------------------|
| Au (4f _{7/2}) | 84.3 |
| Ag $(3d_{5/2})$ | 368.8 |
| $Cu(2p_{3/2})$ | 932.5 |
| Annealed $Cu (2p_{3/2})$ | 932.5 |

Table S2. Ti $2p_{3/2}$ binding energies at P3HT-TiO₂ interface in case of Au, Ag, Cu, and annealed Cu electrode.

| Electrode Metal | Binding Energy (eV) |
|--------------------|------------------------|
| Au | 457.15 |
| Ag | 457.15 |
| Cu | 457.66 |
| Annealed Cu | 457.81 |

| Electrode | V _{oc} (V) | $\frac{J_{sc}}{(mA/cm^2)}$ | Fill Factor (%) | Efficiency (%) |
|-----------|------------------------|----------------------------|--------------------|-------------------|
| Au | 0.28 | 5.87 | 49 | 0.81 |
| Ag | 0.30 | 8.21 | 34 | 0.84 |
| Cu | 0.28 | 9.90 | 44 | 1.21 |
| | | | | |

 Table S3. Photovoltaic parameters of P3HT-PCBM blend solar cells fabricated with different metal electrodes.