Cu/Cu$_2$O nanocomposite films as a p-type modified layer for efficient perovskite solar cells

You-Jyun Chen$^1$, Ming-Hsien Li$^1$, Jung-Chun-Andrew Huang$^{2,4,1}$ & Peter Chen$^{1,3,5}$

Cu/Cu$_2$O films grown by ion beam sputtering were used as p-type modified layers to improve the efficiency and stability of perovskite solar cells (PSCs) with an n-i-p heterojunction structure. The ratio of Cu to Cu$_2$O in the films can be tuned by the oxygen flow ratio (O$_2$/(O$_2$ + Ar)) during the sputtering of copper. Auger electron spectroscopy was performed to determine the elemental composition and chemical state of Cu in the films. Ultraviolet photoelectron spectroscopy and photoluminescence spectroscopy revealed that the valence band maximum of the p-type Cu/Cu$_2$O matches well with the perovskite. The Cu/Cu$_2$O film not only acts as a p-type modified layer but also plays the role of an electron blocking buffer layer. By introducing the p-type Cu/Cu$_2$O films between the low-mobility hole transport material, spiro-OMeTAD, and the Ag electrode in the PSCs, the device durability and power conversion efficiency (PCE) were effectively improved as compared to the reference devices without the Cu/Cu$_2$O interlayer. The enhanced PCE is mainly attributed to the high hole mobility of the p-type Cu/Cu$_2$O film. Additionally, the Cu/Cu$_2$O film serves as a protective layer against the penetration of humidity and Ag into the perovskite active layer.

Since the pioneering work of Prof. Miyasaka$^1$, hybrid organic-inorganic halide perovskite materials have attracted tremendous research interest owing to their inherent photo-electrical properties, making them suitable light absorbers for photovoltaic devices. To date, the highest power conversion efficiency (PCE) of 22.7% has been demonstrated for perovskite solar cells (PSCs)$^5$. The selection of hole transport materials (HTMs) is crucial for effective hole transport from the perovskite structure and the resultant photovoltaic performance$^{3-8}$. High efficiency PSCs usually use organic HTMs such as 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-bifluorene (spiro-OMeTAD), Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), Poly(triarylamine) (PTAA), and Poly(3-hexylthiophene-2,5-diyl) (P3HT). However, their low environmental stability hampers the application of such PSCs. In contrast with organic HTMs, inorganic HTMs are of considerable interest for application in PSCs owing to their long-term stability and high mobility$^6,7$. The use of inorganic HTMs on perovskites can also reduce or even prevent oxygen and water penetration, reducing the degradation rate of the as-formed perovskite$^9-11$. However, the deposition of inorganic HTMs on perovskite must be performed below 100 $^\circ$C, as perovskite is unstable at high temperatures$^{12-18}$. Therefore, the appropriate preparation of HTMs is a key issue in the further development of perovskite solar cells.

Over the past few decades, the electrical, optical, and magnetic properties of cuprous oxide (Cu$_2$O) have been studied extensively$^{19-35}$. CuO$_x$ has been demonstrated as an efficient p-contact for PSCs owing to its good match between its valence bands and perovskite and its promising hole mobility$^{26-30}$. The efficiency was recently improved to 19% in a p-i-n inverted structure using a Cl-doped CH$_3$NH$_3$PbI$_3$ perovskite$^{31}$. However, the CuO$_x$-coated substrate generally suffers a low transmittance in the visible light range below 550 nm and ultrathin CuO$_x$ films are necessary to minimize the optical loss in the inverted structure. It should be noted that much less work has been implemented on inorganic HTMs for use in PSCs with n-i-p structure$^{16,31,32}$. The deposition of HTMs on perovskites is limited because perovskite is vulnerable to high temperatures and polar solvents. In 2016, Nejand et al. demonstrated the production of a uniform, dense, and pinhole-free Cu$_2$O-covered perovskite...
by controlling the tilting angle of the substrate and the deposition power and period via angular rotation of the substrate during the reactive magnetron sputtering process. This angular rotation prevents bombardment damage on the perovskite, but the efficiency of the solar cell only reached 8.93%.10

In this work, we report, for the first time, a p-type Cu/Cu$_2$O and a spiro-OMeTAD layer as combinatorial HTMs in n-i-p heterojunction PSCs to improve the hole extraction capability, device performance, and device stability. For a 20-nm-thick Cu/Cu$_2$O film with an oxygen flow ratio (OFR) of 60%, a high mobility of 60.5 cm$^2$/V·s was obtained, which results in a superior PCE of 17.11% for the PSC, as compared to the standard device with only spiro-OMeTAD as the HTM (PCE of 13.97%). The stability test shows that the Cu/Cu$_2$O layer provides enhanced durability under ambient conditions. Hence, the p-type Cu/Cu$_2$O composite film is a promising HTM modified layer for highly efficient PSCs and a good protection layer for the perovskite active layer. In addition, to meet the demand for energy level alignments in our devices, insertion of the spiro-OMeTAD layer is necessary to prevent damage of the perovskite during the high energy sputtering of the Cu/Cu$_2$O composite layer.

Results
Characterizations of the Cu/Cu$_2$O composite films. Figure 1 shows the X-ray diffraction (XRD) patterns of the ion-beam sputtered Cu/Cu$_2$O composite films deposited on glass over a 5-min period (approximately 20-nm thick) with the OFR ranging from 0 to 60%. The diffraction from pure Cu in the absence of oxygen is shown at the bottom of Fig. 1(a). The characteristic peaks at 43.4°, 50.45°, and 74.05° can be assigned to the Cu (111), (200), and (220) planes, respectively. For the OFR increasing from 10% to 50%, the intensities of the Cu phases are weaken while the Cu$_2$O phase are intensified, suggesting the increasing volume ratio of Cu$_2$O in the nanocomposite films. With further increasing OFR to 60%, there is no visible Cu diffraction and the Cu$_2$O (220) phase dominates. The scanning electron microscopy (SEM) images of the corresponding Cu/Cu$_2$O composite films are provided in the Supporting Information Fig. S1. Owing to the difference in the contrast between Cu and Cu$_2$O, a small number of bright spots were observed for the OFR ranging from 30% to 50%, which are likely associated with the existence of Cu (Supporting Information Fig. S1(c–e)). Smooth morphology with a negligible number of bright spots was observed for the Cu$_2$O film with an OFR of 60%, as shown in the Supporting Information Fig. S1(f), which indicates that most of Cu was oxidized to form Cu$_2$O.

For convenience, the Cu/Cu$_2$O composite films grown under an OFR of X% are denoted as Cu$_2$O$_X$ in the rest of the paper. To determine the elemental composition of the Cu/Cu$_2$O composite films, Auger electron spectroscopy (AES) was performed to monitor the Cu LMM transition, as seen in Fig. 1(b). The peak at 918 eV corresponds to Cu$^0$ bonding for an OFR of 0%. With the increase of OFR, the characteristic AES peak shifts toward lower kinetic energy (917.5 eV for Cu$_2$O$_{40}$ and 917.2 eV for Cu$_2$O$_{50}$), reflecting the increase of the Cu$_2$O component in the composite film. With further increasing OFR to 60%, there is no visible Cu diffraction and the Cu$_2$O (220) phase dominates. The scanning electron microscopy (SEM) images of the corresponding Cu/Cu$_2$O composite films are provided in the Supporting Information Fig. S1. Owing to the difference in the contrast between Cu and Cu$_2$O, a small number of bright spots were observed for the OFR ranging from 30% to 50%, which are likely associated with the existence of Cu (Supporting Information Fig. S1(c–e)). Smooth morphology with a negligible number of bright spots was observed for the Cu$_2$O film with an OFR of 60%, as shown in the Supporting Information Fig. S1(f), which indicates that most of Cu was oxidized to form Cu$_2$O.

To investigate the energy level and the relative position of the Fermi level with respect to the valence band maximum ($\Delta E_{VB}$) of the Cu/Cu$_2$O composite films, ultraviolet photoelectron spectroscopy (UPS) and photoluminescence (PL) spectroscopy were performed, as shown in Fig. 2. Figure 2(a) shows the full UPS spectra and Fig. 2(b) shows a magnification of the spectra near the valence band region from Fig. 2(a). The Au metal rectifies the Fermi energy level position at 0 eV, and the obtained $\Delta E_{VB}$ of the Cu$_2$O$_{60}$ film is 0.55 eV. The corresponding band gap ($E_g$) determined from the UPS spectra (Fig. 2(b)) is 2.07 eV and the work function of Au is approximately 4.7 eV.[11] The peak values in Fig. 2(b) correspond to the energies between the valence band maximum (VBM) and the work function, and the VBM position of the Cu$_2$O$_{60}$ was determined to be approximately −5.25 eV. The conduction band minimum (CBM) of the Cu$_2$O$_{60}$ is −3.18 eV which was determined by the addition of $E_g$ to the VBM. The energy level of the Cu$_2$O$_{60}$ film along with other commonly-used inorganic HTMs is plotted in Fig. 2(d) for comparison. It is noted that the VBM of Cu/Cu$_2$O film is compatible with the other HTMs, suggesting that Cu/Cu$_2$O film can effectively extract the hole carrier from perovskite.

**Figure 1.** (a) XRD profiles of the Cu$_2$O films deposited at different OFRs from 10% to 60%. The pure Cu (OFR = 0%) film is also shown for comparison. (b) AES of pure Cu, Cu$_2$O powder and Cu/Cu$_2$O composite films deposited under OFRs of 40%, 50%, and 60%.
The electrical properties of the Cu/Cu₂O composite films were analyzed by Hall effect measurements and a four-point probe method, and are summarized in Table 1. Figure S2 presents the Hall effect measurements of Cu/Cu₂O composite films at variant OFRs. The Cu₂O₄₀, Cu₂O₅₀, and Cu₂O₆₀ films have been determined to be p-type semiconducting materials. As evidenced from the Hall effect measurements shown in Fig. S2(a), for OFR = 30% the Cu/Cu₂O composite film is a n-type semiconductor, which is not of interest for HTM application. The Cu₂O₆₀ film is nearly insulating (sheet resistance ~83 kΩ/square) owing to the high volume ratio of Cu₂O. The sheet resistances of the Cu₂O₄₀ and Cu₂O₅₀ films are 72.5 and 210.1 Ω/square, respectively, and the corresponding hole mobilities are 1.87 and 1.23 cm²/V-s, which are at least three orders of magnitude higher than the organic hole transport layers of spiro-OMeTAD (1.6 × 10⁻⁴~1.6 × 10⁻³ cm²/V-s). Notably, the hole mobility of the Cu₂O₆₀ film is as high as 60.5 cm²/V-s. The hole carrier concentrations of the Cu₂O₄₀, Cu₂O₅₀, and Cu₂O₆₀ films are 2.3 × 10²², and 6.19 × 10¹⁷ cm⁻³, respectively.

X-ray photoelectron spectroscopy (XPS) was employed to analyze the chemical compositions of the composite Cu/Cu₂O films grown with different OFRs. Figure 3(a–d) show the XPS spectra of Cu 2p₃/₂ core level. All the films exhibit characteristic peaks at 932.3 eV and 933.1 eV that are respectively corresponding to copper(I) oxide and copper metal as reported in the literature. By deconvoluting the signal and integrating the individual area, the ratio of Cu to Cu₂O for Cu₂O₃₀, Cu₂O₄₀, Cu₂O₅₀ and Cu₂O₆₀ films are estimated to be 0.79, 0.50, 0.22 and 0.05, respectively. The Cu/Cu₂O ratio as a function of oxygen flow ratios is shown in Fig. 3(e), indicating that the Cu content decreases with the oxygen flow. The tendency of Cu content in the sputtered film is consistent with the SEM results.

Table 1. Electrical properties of the Cu/Cu₂O films under different oxygen flow ratios (OFRs) and that of spiro-OMeTAD for comparison.

| OFR (%) | Thickness (nm) | Type | Sheet Resistance (Ω/square) | Mobility (cm²/V-s) | Bulk Concentration (cm⁻³) |
|---------|----------------|------|-----------------------------|-------------------|----------------------------|
| 40      | 20             | p    | 72.5                        | 1.87              | 2.3 × 10²²                  |
| 50      | 20             | p    | 210.1                       | 1.23              | 1.54 × 10²²                 |
| 60      | 20             | p    | 83360                       | 60.5              | 6.19 × 10¹⁷                 |
| spiro-OMeTAD/tBP/LiTFSI | 100–200       | p    |                             | 1.6 × 10⁻⁴       | 1.6 × 10⁻³                  |

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Devices. The device architecture is based on the n-i-p heterojunction configuration which is composed of FTO/cp-TiO₂/mp-TiO₂/CH₃NH₃PbI₃/spiro-OMeTAD/Cu₂Oₓ/Ag, as shown in Fig. 4(a). The standard (reference) device is the one without the Cu₂Oₓ film interlayer. The active layer of the CH₃NH₃PbI₃ perovskite was prepared by solvent engineering³⁷, while the Cu₂Oₓ interlayer was grown by sputtering on a Cu target by tuning the OFR over a 5 min period. The thickness of the Cu₂Oₓ films are approximately 20 nm, as estimated by the cross-sectional SEM images (cf. Fig. S1 in Supporting Information). For convenience and clarity, the energy level diagram of the device is depicted in Fig. 4(b).

Figure 5(a) shows the current density-voltage (J-V) curves of the Cu₂Oₓ based perovskite solar cells (with active area of 0.09 cm²) prepared with varying OFRs, and the corresponding photovoltaic parameters are summarized in Table 2. Amongst these devices, the Cu₂O₆₀ device had a short circuit current density (J_sc) of 22.46 mA/cm², open circuit voltage (V_oc) of 1.03 V, and fill factor (FF) of 74.1%, resulting in the best PCE of 17.11% under AM 1.5 G illumination. Produced under similar fabrication conditions, the PSCs incorporating Cu₂O₄₀ and Cu₂O₅₀ layers show J_sc of 21.52 and 21.97 mA/cm², V_oc of 1.03 and 0.95 V, FFs of 73.18 and 72%, and PCEs of 16.21 and 14.98%, respectively. The reference device without Cu₂Oₓ showed a J_sc of 19.02 mA/cm², V_oc of 0.997 V, FF of 73.63%, and PCE of 13.97%. The incorporation of the Cu₂Oₓ interlayer serves as a bridge between the organic HTM (spiro-OMeTAD) and the metal electrode (Ag), and facilitates hole transport in the device owing to the high hole conductivity of the Cu/Cu₂O composite films. Notably, the electron mobility of

![Figure 3](https://www.nature.com/scientificreports/)
TiO$_2$ ranges from 0.1–10 cm$^2$/V-s$^{38,39}$, while the hole mobility of Cu$_2$O$_X$ is typically between 1–60.5 cm$^2$/V-s. Unbalanced ambipolar transport may be the main cause of the hysteresis observed in the prepared devices$^{40–42}$. The introduction of spiro-OMeTAD not only protects the perovskite active layer during sputtering deposition but also acts as an electron blocking layer, as schematically illustrated in Fig. 4(b). Figure 5(b) shows the incident photon-to-electron conversion efficiency (IPCE) spectra of the four fabricated devices. The devices with Cu$_2$O$_{40}$ and Cu$_2$O$_{50}$ layers show good responses with maximum values of approximately 80% in the range of 400 to 700 nm. The IPCE is approximately 90% for the Cu$_2$O$_{60}$ incorporated device over the same wavelength range. The IPCE spectra reveal that the Cu$_2$O$_{40}$, Cu$_2$O$_{50}$, and Cu$_2$O$_{60}$ incorporated devices yield higher responses and photocurrents than the standard device. Figure S3 (Supporting Information) shows the statistical distribution of the photovoltaic parameters resulted from 15 devices for Cu$_2$O$_{60}$-based PSCs as well as 15 standard devices for comparison. The results show that the Cu$_2$O$_{60}$-based device exhibits better efficiency than the reference devices. We further enlarge active area of 2.06 cm$^2$ for Cu$_2$O$_{60}$ based perovskite solar cell which exhibits a J$_{sc}$ of 21.66 mA/cm$^2$, V$_{oc}$ of 1.0 V, FF of 42.47%, and PCE of 9.22% and its corresponding J-V curve is shown in Supporting Information Fig. S4. It can be found that the device with large 2.06 cm$^2$ active area is lower than that of the smaller 0.09 cm$^2$ active area ones due to the poor FF. The reducing FF is mainly resulted from the increasing sheet resistance of FTO substrate that raises the probability of the charge recombination before carrier extracted by electrode$^{43,44}$.

**Table 2.** Photovoltaic parameters of the Cu$_2$O-based perovskite solar cells with varying OFRs. The standard spiro-OMeTAD device without Cu$_2$O is shown for comparison.

| Device (0.09 cm$^2$) | V$_{oc}$ (V) | J$_{sc}$ (mA/cm$^2$) | FF (%) | PCE (%) | Rs (Ω) | Rsh (Ω) |
|---------------------|-------------|---------------------|--------|---------|-------|--------|
| w/o Cu$_2$O         | 0.997       | 19.02               | 73.63  | 13.97   | 48.81 | 14.8k  |
| Cu$_2$O$_{40}$      | 1.03        | 21.52               | 73.18  | 16.21   | 79.13 | 16.36k |
| Cu$_2$O$_{50}$      | 0.95        | 21.97               | 72.0   | 14.98   | 53.99 | 2.77k  |
| Cu$_2$O$_{60}$      | 1.03        | 22.46               | 74.1   | 17.11   | 60.68 | 6.95k  |

**Figure 4.** (a) Device illustration and (b) the corresponding band diagram of the general device architecture.

**Figure 5.** (a) J-V characteristics of perovskite solar cells without and with Cu$_2$O$_X$ (X = 40, 50 and 60) for active area of 0.09 cm$^2$. (b) IPCE curves and integrated current density for corresponding PSCs.
Stability Test. Finally, we monitor the long-term device stability of the normalized efficiency for the encapsulated Cu$_2$O$_{60}$-based devices along with the standard cell and the results are shown in Fig. 6(a). When stored in the dark, the efficiency of the standard device drops rapidly after 12 days, while the devices with the Cu/Cu$_2$O composite films show long-term stability for at least 30 days. The results demonstrate that p-type Cu/Cu$_2$O composite films are promising candidates for the modification of the HTM property for high efficiency PSCs, while simultaneously acting as a protecting layer. The devices with the Cu/Cu$_2$O composite film were transferred to a light soaking condition (one sun illumination). The aging test indicated that approximately 67% of the initial efficiency is retained after 50 h, as shown in Fig. 6(b).

Discussion
In summary, p-type Cu/Cu$_2$O composite films with a tunable Cu/Cu$_2$O ratio were fabricated by controlling the oxygen flow rate during the ion beam sputtering of Cu targets. The resistance and mobility of the Cu/Cu$_2$O composite films can be controlled to optimize the device performance of the PSCs with an n-i-p heterojunction configuration. In comparison to the standard device, the PCEs of the devices incorporating Cu/Cu$_2$O composite films are significantly improved. Furthermore, the Cu/Cu$_2$O composite films can effectively protect the perovskite active layer and enhance the lifetime of the PSCs.

Methods
Fabrication of standard perovskite solar cells. The fluorine-doped tin oxide (FTO) glass was etched with zinc powder and hydrochloric acid (1 M) to house two electrodes, which were cleaned by an ultrasonic soap, water, and ethanol bath and then rinsed with deionized water. A 70-nm-thick TiO$_2$ compact layer (cp-TiO$_2$) was deposited on the cleaned FTO substrates by spray pyrolysis of a titanium diisopropoxide bis(acetylacetonate) (75 wt.% in isopropanol, Aldrich) precursor solution diluted in ethanol (1:39 v:v), at 485 °C for 30 min. This was followed by the deposition of a 20 mM TiCl$_4$ solution layer, which functions as an electron transport layer (ETL). The mesoporous TiO$_2$ layer (mp-TiO$_2$) was formed by spin-coating a diluted TiO$_2$ solution (1:8.5 v:v) at 4000 rpm for 30 s followed by sintering at 500 °C for 30 min. The CH$_3$NH$_3$PbI$_3$ precursor was prepared inside a nitrogen-filled glove box with oxygen and moisture levels <1 ppm by mixing 0.288 g of CH$_3$NH$_3$I (dyesol, 99.99%) with 0.831 g of PbI$_2$ (Aldrich, 99.999%, ultra-dry) in a 1:1 equimolar ratio. The components were dissolved in a mixture of γ-butyrolactone (GBL) and dimethyl sulfoxide (DMSO) (6:4 v:v) and heated at 50 °C under stirring for 12 h for complete dissolution. CH$_3$NH$_3$PbI$_3$ was then spin-coated onto the FTO/cp-TiO$_2$/mp-TiO$_2$ substrate at 1000 rpm for 10 s and at 5000 rpm for 30 s, and the anti-solvent toluene was injected for 15 s in the second spin step. The spin-coated perovskite film was dried at 100 °C for 10 min to remove the toluene. The spiro-OMeTAD solution was prepared by dissolving 72.3 mg of spiro-OMeTAD, 28.8 μL of tert-butylpyridine (tBP), and 17.5 μL of lithium-bis(trifluoromethanesulfonyl)imide (Li-TFSI) (from a stock solution of 520 mg/mL of Li-TFSI in acetonitrile (Aldrich, 99.8%)) in 1 mL of chlorobenzene. The spiro-OMeTAD solution was then spin coated onto the MAPbI$_3$ substrate at 4000 rpm for 20 s. Finally, a 60-nm-thick silver layer was thermally evaporated to form the counter electrode.

Fabrication of Cu$_2$O-based perovskite solar cells. The MAPbI$_3$ substrates were fabricated as described above. The spiro-OMeTAD serves as a buffer layer, and an ion beam sputtering system was used to deposit the Cu/Cu$_2$O films. The vacuum chamber was evacuated to a base pressure of 2.2 × 10$^{-6}$ torr. A copper substrate (99.99% purity) was used as the sputtering target. The Cu/Cu$_2$O films were grown at room temperature (~30°C) with different Ar and O$_2$ flow rates.

Characterization. The crystallographic properties of the films were determined by grazing incidence X-ray diffraction using Cu Kα radiation ($\lambda = 1.5418$ Å, D8, Bruker, Germany) at room temperature with a scanning step...
size of 0.005°. The surface morphology and cross-section of the samples were analyzed by field-emission scanning electron microscopy (SUPRA® 55). The carrier type, carrier concentration, and electrical resistivity were measured using a four-terminal van der Pauw configuration at room temperature. The UPS and XPS experiment were performed at beamline 24A of the Taiwan Light Source in the National Synchrotron Radiation Research Center (NSRRC). A microscopic PL system (MRI, Protrustech Co., Ltd., Taiwan) was used to determine the band gap of the films with a pumping wavelength of 532 nm. The J-V measurement was performed using a solar simulator (SS-F5-3A, EnliTech) with AM 1.5 G spectra and the device was connected to a source meter (Keithley 2401) for recording the J-V data. The light intensity was calibrated using reference silicon solar cells to be 100 mW/cm². The scan rate was 1 V/s for the forward scan (from J_0 to V_0). A metal mask with an aperture size of 0.09 cm² was used to define the active area. A 300 W intensity monochromatic (Newport Cornerstone 260) xenon lamp (Newport) and a source meter (Keithley 2401) were integrated to measure the IPCE response of the devices.

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Author Contributions

Prof. J.C.A. Huang and Prof. Peter Chen contributed to the conception and design of the research and experiment. Y.J. Chen and M.H. Li carried out film preparation and characterization, device fabrication and performance measurements. Y.J. Chen analyzed data and wrote the manuscript with the assistance of Dr. M.H. Li, Prof. J.C.A. Huang, and Prof. Peter Chen. All authors reviewed the manuscript.

Additional Information

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