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Low-cost electrodes for stable perovskite solar cells

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Cost-effective production of perovskite solar cells on an industrial scale requires the utilization of exclusively inexpensive materials. However, to date, highly efficient and stable perovskite solar cells rely on expensive gold electrodes since other metal electrodes are known to cause degradation of the devices. Finding a low-cost electrode that can replace gold and ensure both efficiency and long-term stability is essential for the success of the perovskite-based solar cell technology. In this work, we systematically compare three types of electrode materials: multi-walled carbon nanotubes (MWCNTs), alternative metals (silver, aluminum, and copper), and transparent oxides [indium tin oxide (ITO)] in terms of efficiency, stability, and cost. We show that multi-walled carbon nanotubes are the only electrode that is both more cost-effective and stable than gold. Devices with multi-walled carbon nanotube electrodes present remarkable shelf-life stability, with no decrease in the efficiency even after 180 h of storage in 77% relative humidity (RH). Furthermore, we demonstrate the potential of devices with multi-walled carbon nanotube electrodes to achieve high efficiencies. These developments are an important step forward to mass produce perovskite photovoltaics in a commercially viable way. *Published by AIP Publishing.*

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The latest record power conversion efficiency of perovskite solar cells places this technology close to the lab performance of commercial thin-film technologies as copper indium gallium selenide and cadmium telluride and CdTe.¹ Along with the high power conversion efficiencies, perovskite devices can be solution-processed² at low cost using inexpensive absorber and charge transport materials.³ However, the current best performing lab-scale devices mostly utilize Au as the top electrode material,⁴ which significantly increases the overall costs of perovskite solar cells and is not suitable for large scale production. Therefore, alternative low-cost electrodes that can ensure efficient and stable devices are desirable for the commercialization of this technology. So far, a number of electrode materials have been investigated to replace Au, which can be broadly divided into three categories: alternative metals to Au, oxides, and carbon-based electrodes (Refs. 5–18).

Metallic alternatives to Au, such as Ag,^{5,6} Al,^{7,8} and Cr,⁹ are generally less expensive but still guarantee high initial performance due to their high reflectivity and conductivity. However, some of these less expensive metals have been shown to reduce the stability of the devices.^{8,10,11} In contrast to metals, oxides have refractive indexes closer to perovskites, resulting in less reflection at the electrodes and, consequently, lower photocurrent for the same absorber thickness. On the other hand, they are promising for device

stability.^{12,13} Semi-transparent oxides have been demonstrated as electrodes by themselves,¹² sometimes with additional metal layers to enhance device performance.^{13,14} Carbon-based electrodes like graphene,¹⁵ carbon nanotubes,¹⁶ and carbon nanotube composites¹⁷ are also not as reflective as metals but can reach competitive power conversion efficiencies¹⁸ and can potentially lower device costs as they are solution processable. A direct comparison of these three types of gold replacements based on the literature alone is impossible because of the extreme sensitivity of the devices to the fabrication conditions (different from lab to lab) that influence both performance and stability. A fair comparison requires the devices with the different electrodes to be produced and tested side-by-side at the same location. Yet, even if these production and testing requirements are met, the identification of the best Au replacement electrode is not straightforward because the electrodes influence the electro-optical properties, stability, and costs of the device simultaneously. Therefore, to find an adequate replacement for Au, all these parameters should be taken into account simultaneously.

The suitability of different electrodes to replace Au can be readily evaluated by shelf-life testing at high relative humidity (RH). There are some reports in the literature of moisture catalysing degradation reactions between the electrode and methylammonium lead iodide (CH₃NH₃PbI₃).^{8,10,11} Furthermore, even if CH₃NH₃PbI₃ is not degraded by reaction with the electrode, it will still degrade irreversibly if biased in an

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environment with moisture.¹⁹ Thus, shelf-life testing at high RH provides insights into the long-term stability of the device depending on whether the electrode is reactive and whether it will protect the $\text{CH}_3\text{NH}_3\text{PbI}_3$ from detrimental moisture.

In this work, we benchmark devices with alternative electrode materials: metals, oxides, and carbon nanotubes against Au electrodes. Devices are compared in terms of efficiency, long-term stability, and cost. We base our experiments on devices with the following device architecture: ITO/ TiO_2 / $\text{CH}_3\text{NH}_3\text{PbI}_3$ /doped N2, N2', N2', N2', N7, N7, N7', N7'-octakis (4-methoxyphenyl)-9, 9'-spirobi (9H-fluorene)-2, 2', 7, 7'-tetramine (spiro-OMeTAD)/electrode²⁰ [Fig. 1(a)], which is optimized for Au. For the sake of comparison, the device architecture is kept constant, and only the electrode material is changed [Fig. 1(a)]. The metallic electrodes (Au, Ag, Al, and Cu) are thermally evaporated either directly on top of spiro-OMeTAD or on spiro-OMeTAD covered with a sputtered indium tin oxide (ITO) layer. A purely ITO electrode is chosen to represent the oxides. A multi-walled carbon nanotube (MWCNT) electrode represents the carbon-based materials. The MWCNTs are spray-coated with and without an ITO. The stability of the resulting devices is determined by high humidity shelf-life testing, i.e., storing devices in the dark at 77% RH for up to 180 h. The reference devices with a gold electrode have an initial power conversion efficiency (η) of $14.6 \pm 0.7\%$, an open-circuit voltage (V_{oc}) of 950 ± 15 mV, a short-circuit current density (J_{sc}) of 21.1 ± 0.1 mA cm^{-2} , and a fill factor (FF) of $73 \pm 3\%$. Details on the device performance, fabrication, and characterization of devices with the other electrodes can be found in the [supplementary material](#).

Replacing Au directly with the less expensive metal alternatives such as Ag, Al, and Cu reduces the initial efficiency of the devices [Figs. 1(b) and S1, [supplementary material](#)]. The rather low efficiency of devices with Ag, Al, and Cu is suggested to be caused by the diffusion and subsequent detrimental chemical reaction of these metals with the spiro-MeOTAD and/or $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer. When an ITO layer (150 nm, $69 \Omega/\square$), that can act as a diffusion barrier, is added between the metal and the spiro-OMeTAD, the devices reach efficiencies comparable to Au electrodes [Fig. 1(b), and Table S1, [supplementary material](#)]. These high efficiencies

are attributed to devices with ITO/metal electrodes benefiting from the high reflectivity of the metals, while any reaction with the spiro-MeOTAD and/or $\text{CH}_3\text{NH}_3\text{PbI}_3$ is prevented by the ITO. Conversely, reference devices with only ITO electrodes have a lower J_{sc} . The lower J_{sc} is explained by the lower reflectivity provided by the ITO electrode compared with Au.

The finding of an Au alternative with similar performance motivates the examination of their stability. To assess the stability, we track the performance of the devices stored in high humidity shelf-life conditions, i.e., stored at 77% RH in the dark [Fig. 1(b)]. Devices with solely Au or ITO exhibit gradual decrease in performance. This drop is primarily due to a J_{sc} loss. We attribute this loss of photocurrent to regions of water vapour ingress where the $\text{CH}_3\text{NH}_3\text{PbI}_3$ hydrates and no photocurrent is generated after this reaction (see Fig. S2, [supplementary material](#)). Conversely, devices with the ITO layers and alternative metals fail in the first 100 h, displaying signs of material decomposition (Fig. S2, [supplementary material](#)). Our observations agree with previous reports that moisture induces irreversible degradation reactions between the $\text{CH}_3\text{NH}_3\text{PbI}_3$ and electrodes containing Ag or Al.^{10,11} We note that ITO covers only the spiro-OMeTAD in the metal region, leaving areas between the electrodes uncovered, which may provide pathways for diffusion of the metals. Nevertheless, degradation will always occur if the interlayer is not pinhole-free. Thus, a non-metallic electrode material, preferably inert and impermeable to water vapour, is required for long-term device stability.

Graphene and graphene-like materials as multi-walled carbon nanotubes (MWCNTs) are known for being chemically inert²¹ and can potentially enhance the stability of perovskite devices. Moreover, MWCNTs can be made at large scale inexpensively²² and deposited by solution based processes, further reducing the costs of device fabrication. We integrated the ultrasonic spray coating process of MWCNT inks through shadow masks, developed previously,²³ to generate patterned electrodes on devices without any post-deposition treatment. The previously optimised formulation was used for the deposition of compact MWCNT electrodes [Fig. 2(a)] with and without the ITO layer. The MWCNT layers have a sheet resistance of approximately $50 \Omega/\square$ (MWCNT films on glass, Table S2, [supplementary material](#)), which is approximately two orders of

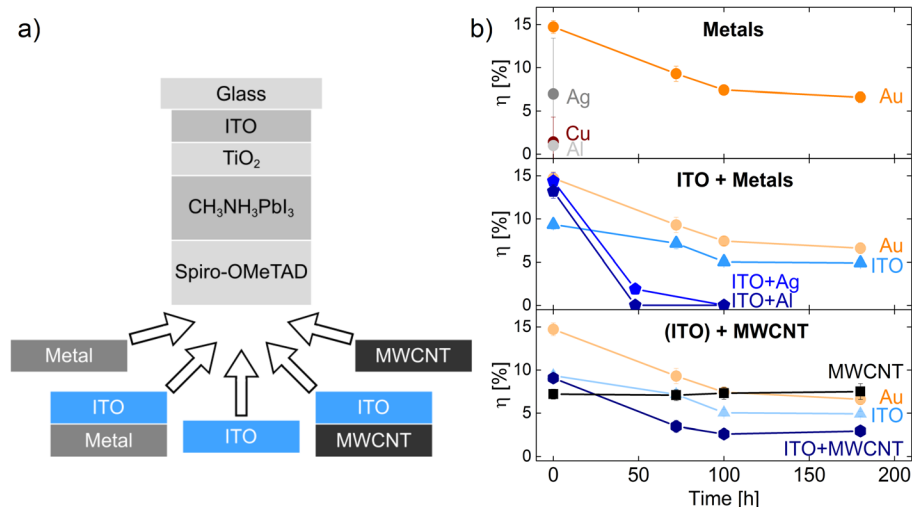


FIG. 1. Benchmarking of the stability of perovskite solar cells with various types of back electrodes. (a) Layer stack scheme of the perovskite solar cell. (b) Power conversion efficiency (η) of samples with different contacts at progressive times stored at 77% RH.

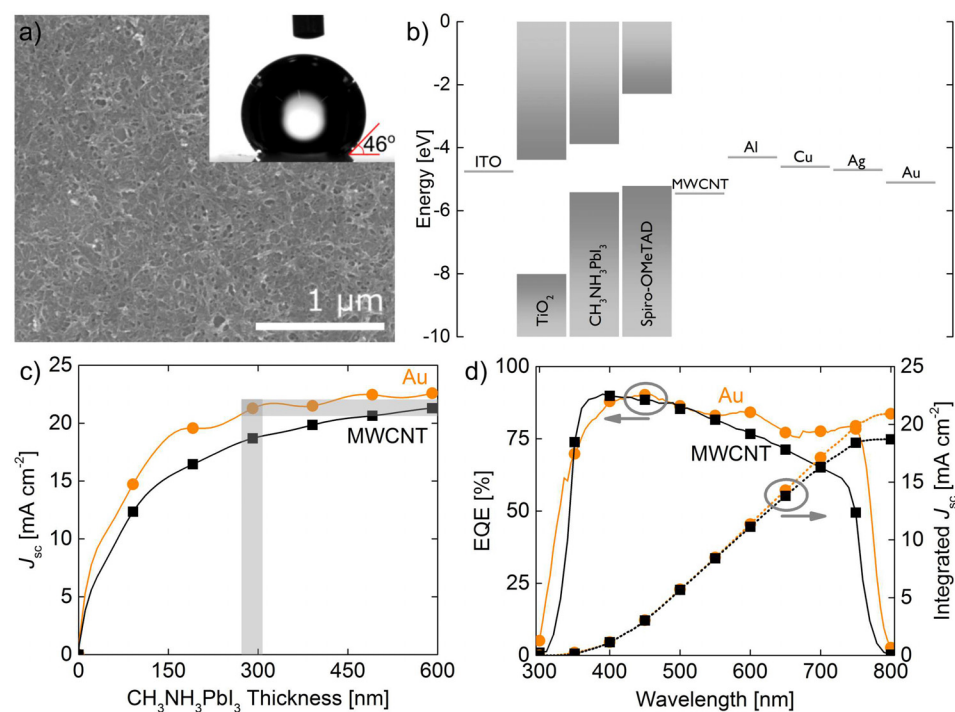


FIG. 2. Top morphology of the MWCNT layer, energy levels of the materials used in this work, and comparison of J_{sc} and External Quantum Efficiency (EQE) between devices with Au and MWCNT contacts. (a) Scanning electron microscopy of MWCNTs on a device. Inset: contact angle measurement on the MWCNT contact; (b) energy levels of the materials used in this work; (c) Simulated J_{sc} of devices with Au (yellow circles), ITO/Ag (dark blue triangles), and MWCNT cathodes (black squares); and (d) EQE and short-circuit current of devices with Au and MWCNT contacts.

magnitude larger than typically measured for evaporated metals.²³ Devices with the non-reflective MWCNT electrodes, and without the ITO layer, have an average efficiency of 7.1% (best device 8.5%). This reduced efficiency of the perovskite solar cells with MWCNTs, compared to Au, is mostly due to a low FF (40%) that is attributed to the injection barrier for hole injection from spiro-OMeTAD into the MWCNTs [Fig. 2(b)]. We rule out the hypothesis of the low FF being due to the sheet resistance of the MWCNT, because ITO films have a higher sheet resistance than the MWCNT, but the devices with ITO electrodes have higher FF (Table S2, [supplementary material](#)). Another source of efficiency loss for devices with MWCNTs is the low reflectivity of these electrodes (Fig. S2, [supplementary material](#)), which limits the total amount of generated charges [Figs. 2(c) and 2(d)]. The addition of an ITO layer between the MWCNT and spiro-OMeTAD increases both FF and J_{sc} , resulting in an efficiency of 8.8%. The introduction of the ITO improves hole injection to a small extent, as noted from the slight FF improvement. The slight J_{sc} increase with the introduction of ITO is explained by an increase in the refractive index mismatch that enhances reflection at the back electrode.

The shelf-life testing shows that humidity has no effect on the devices with solely MWCNT electrodes [Fig. 1(b)]. In contrast, the efficiency of devices with the ITO/MWCNT electrode decreases at the same rate as in the devices with solely ITO or Au as the electrode. The unchanged performance of the devices with the MWCNT electrode together with no visual indications of the formation of hydrated $\text{CH}_3\text{NH}_3\text{PbI}_3$ upon high RH storage (Fig. S2, [supplementary material](#)) suggests that the MWCNT electrode is not only hydrophobic [see inset Fig. 2(a)] but also impedes the penetration and diffusion of water vapour into the device. Nonetheless, the water-vapour barrier properties of MWCNTs seem to require direct contact between the MWCNTs and spiro-OMeTAD, because devices with ITO-MWCNTs do hydrate. Since MWCNT electrodes

are good barriers for both vapour and liquid water, we analyse the competitiveness of this electrode against the others considered in this work. The material costs directly determine the commercial viability of the technology, so even an electrode that guarantees stability can be ruled out for being too costly. In Fig. 3, we show the material cost of the electrodes per area (see Table S3, [supplementary material](#)) vs. the device performance after 180h of high humidity testing to judge if the enhancement in stability would be economically justifiable. The MWCNTs have some of the lowest material costs and retain the efficiency of the devices over the 180h of testing, making them the most cost effective electrode evaluated. If the initially low (relative to reflective metal electrodes) power conversion efficiency of devices with MWCNTs could be increased to a point comparable to the metals, these carbon-based materials offer high viability.

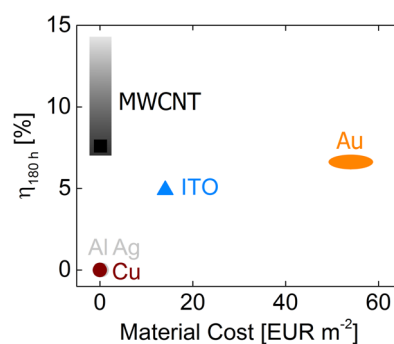


FIG. 3. Cost vs. stability of the perovskite electrodes for various electrodes. Power conversion efficiency after 180h storage at 77% RH (η_{180h}) vs. the material cost required for: an electrode sheet resistance of $10\Omega/\square$, for MWCNT and ITO, or to achieve an average reflectivity above 80% in the visible, for Al, Ag, Cu, and Au (Fig. S2, [supplementary material](#)): Black shading indicates gains possible with the strategies outlined to improve the efficiency of devices with MWCNT electrodes. The most desirable electrode materials are located in the top-left corner of the graph.

Having demonstrated that the MWCNTs are more stable and much cheaper than Au electrodes, we discuss in the following paragraph strategies to further enhance the efficiencies of the perovskite solar cells with MWCNT electrodes. In this regard, it shall be noted that in this work, the architecture of the perovskite solar cell was optimized for Au electrodes. However, as Tait *et al.* demonstrated already for organic solar cells, identical *FFs* can be achieved with MWCNT and noble metal electrodes.²³ Therefore, three changes of the architecture are required: (i) reduction of the electrode resistance by alignment of the work function of MWCNTs with the HOMO of the hole transport layer, i.e., of spiro-OMeTAD, (ii) reduction of the sheet resistance of the MWCNT layer by increasing its thickness/density, and (iii) increase in the thickness of the perovskite layer above 600 nm to reduce the impact of the lower reflectivity of the MWCNT electrode [see Fig. 2(c)]. If these strategies are successfully implemented, devices with MWCNT electrodes with the current architecture should reach the same efficiencies as the best devices produced in this work with Au, i.e., around 15.4%. This value is in pair with the recent report of devices with 15.6% η using a carbon cloth electrode¹⁸ and just above the 14.7% obtained with a carbon nanotube-based electrode.¹⁷

In summary, we demonstrate that by changing the electrode of perovskite solar cells from Au to MWCNT we reduce heavily the material costs and simultaneously maintain a much higher power conversion efficiency when the devices are exposed to humidity. Although initial power conversion efficiencies of the devices with MWCNT electrodes are yet lower compared to Au electrodes, they retain their efficiency even after 180 h of storage at high humidity, exceeding the performance of Au and any other metal electrode which shows strong degradation. We also indicate that devices with MWCNTs have the potential to match the current efficiencies of devices with Au electrodes, if the device architecture and electrode layers are further optimized towards MWCNTs as electrode materials. Furthermore, we demonstrate that the utilization of metals, oxides, or combinations of both requires thorough packaging to guarantee long term stability of the devices. Overall, MWCNTs are the electrodes that offer the best possibility for perovskite solar cells to achieve viable large scale production.

See [supplementary material](#) for details on device fabrication and characterization; the detailed device parameters with the different electrodes; transmittance, reflectance, and sheet resistance of the contacts; micrographs of the devices after 180 h of testing at high relative humidity; and values used to compare the performance of the devices.

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¹See <http://www.nrel.gov/ncpv/> for the certified record efficiencies of the different photovoltaic technologies.

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